

CATALYSED OXIDATION OF SOME ORGANIC SUBSTANCES

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Harsh Vardhan Singh



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C E R T I F I C A T E

This is to certify that the thesis entitled "Catalysed Oxidation of some Organic Substances" submitted for the Degree of Doctor of Philosophy of the University of Bundelkhand, Jhansi (U.P.) is a record of bonafide research work carried out by Sri Harsh Vardhan Singh under my guidance and supervision.

The work embodied in this thesis or a part thereof, has not been submitted for the award of any other Degree or Diploma. All the help and assistance received during the course of present investigations have been duly acknowledged.

R. K. Shukla

Raj Kishore Shukla

M.Sc. Ph.D.

Head, Chemistry Department

Atarra Post - Graduate College

Atarra (Banda)

U.P.

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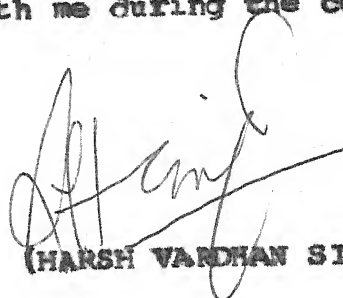
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C_H_A_P_T_E_R - I

I_N_T_R_O_D_U_C_T_I_O_N

Application of kinetic data for the study of the mechanism of a chemical reaction has been a subject of interest to several chemists because it has wide application in connection with the understanding of the salient, electronic, structural and stereochemical features of a chemical process. The importance of a kinetic study for a chemist lies in the fact that by understanding the dependence of various rates on reaction variables (concentration, temperature, solvent etc.) one can control the course and products of a reaction and thus the conditions required for favouring a desired product can be successfully predicted. The numerous scientific publications of the difficult and careful observations and precise interpretation of the kinetic data are perhaps the surest criteria of chemist's present interest in kinetics.

A few important factors which are helpful in determining the mechanism of a redox process, are order of the reaction with respect to oxidant, reductant, alkali or acid and catalyst if any, effect of ionic strength of the medium, solvent variation, temperature variation, thermodynamic parameters etc. The identification of the reaction product is another important factor, which leads to the elucidation of the reaction mechanism.

Several redox reagents have been utilized from time to time for over all as well as step by step redox reactions. The most commonly used redox reagent, are inorganic ions as permanganate, dichromate, peroxydisulphate, hexacyanoferrate (III), cerium (IV) and vanadium (V). Some less familiar inorganic redox reagents are iodine monochloride, Mn (III), Cu (III), Pb (IV), Co (III),

Sn (II), Au (III), and Ag (III) etc. The organic redox reagents are N - Chlorosuccinimide, N - bromosuccinimide, N - chloro - benzamide, chloramine - T etc. In recent publications¹, Bomford and Tipper have given a detailed account of several familiar and less familiar redox reagents. Berba and coworkers² have also described new redox titrants in another publications.

1.1 : LITERATURE SURVEY ON CHLORAMINE - T AND HEXACYANOFERRATE (III) OXIDATION

The present thesis deals with the studies of chloramine T oxidation of p - hydroxy and m - hydroxy benzoic acids in alkaline media using osmium tetroxide as catalyst and hexacyanoferrate (III) oxidation of 4 - butyl morpholine and morpholine butanol in aqueous alkaline media in presence of osmium tetroxide as catalyst. Some works on chloramine - T and hexacyanoferrate (III) are given below.

Chloramine - T is the sodium salt of N - chloro - 4 - methyl benzene sulphonamide ($\text{CH}_3\text{C}_6\text{H}_4\text{SO}_2\text{N NaCl} \cdot 3\text{H}_2\text{O}$) and is a very potent oxidising agent in alkaline as well as in acidic media.³ It has been used for the oxidation and estimation of various inorganic substances.⁴⁻¹⁴ The organic sulphur compounds¹⁵⁻ are qualitatively oxidised by chloramine - T. Mahadevappa and co - workers have also estimated large number of compounds.²²⁻³¹ They have also estimated unsaturated alcohols such as allylic alcohols,³²⁻³³ crotyl alcohol³⁴ and cinnamyl alcohol.³⁵ Chloramine - T also reacts with α - amino acids.³⁶

Chloramine - T oxidation of hydrogen peroxide³⁷ glycerol³⁸, p - cresol³⁹, some ketones,⁴⁰ α - aminoacids⁴¹⁻⁴²

E D T A⁴³, aniline⁴⁴ and phenols⁴⁵ alcohols⁴⁶, aldehydes⁴⁷, dimethyl sulphoxide⁴⁸ have been reported.

Recently, Santappa et al⁴⁹ have studied the oxidation of cinnamic acid crotonic acid by chloramine - T. Very recently, Mahadevappa and co-workers⁵⁰ have studied the oxidation of glutamine and Sarine by chloramine - T. They have also studied the kinetics of oxidation of amino acids⁵¹ by chloramine - T in HCl medium at 30°C. The reaction shows first order dependence each with respect to hydrogen ion and oxidant and is independent of the concentration of substrate. A review with reference on the estimation and oxidation kinetics of several compounds by chloramine - T has been published.⁵²

Chloramine - T thus involves a variety of kinetics depending upon the nature of substrate involved, presence or absence of a catalyst. Singh and coworkers have recently studied the oxidation kinetics of some ketones⁵³ by chloramine - T.

Oxidation of organic substrates in alkaline medium by hexacyanoferrate (III) has received much attention in recent years due to its cheap availability and less complexity involved in the oxidation reactions. A number of relatively fast reactions involving hexacyanoferrate (III) have been studied in alkaline media⁵⁴⁻⁵⁶. Oxidation of hydrazine by hexacyanoferrate (III) in alkaline solution leads quantitatively to the formation of nitrogen⁵⁷ and kinetic studies reveal first order dependence on hexacyanoferrate (III) and N_2H_2 concentration. Kinetics of oxidation of sulphite ion by alkaline hexacyanoferrate (III)

ion was studied by Krishna and Singh.⁵⁸ They reported first - order dependence of the reaction on sulphite and hexacyanoferrate (III) ion. Extensive work has been done on the hexacyanoferrate (III) ion oxidation of sugars by Singh and Coworkers in alkaline media⁵⁹ and they have reported zero - order dependence on both, sugars and hydroxyl ion concentration. Singh and coworkers⁶⁰ favoured electron transfer process in oxidation of formaldehyde. Views of water and coworkers were completely modified and complex mechanism was ruled out in recent publication.⁶¹ Recently, Singh and coworkers have studied the oxidation of levulinic acid⁶² and morpholine.⁶³

Homogeneously catalysed processes find their little use in synthetic work. The homogeneously catalysed biological reactions are still putting challenge to scientists. A very interesting and effective catalyst for the oxidation of organic compounds in solution is osmium tetroxide. Griegee⁶⁴ showed that the reaction involved as Osmium (VI) intermediate which can be isolated in many cases. Solymosi⁶⁵ studied a number of substrates using hexacyanoferrate (III) as an oxidant in presence of osmium tetroxide as catalyst, but no kinetic result was reported until 1966. Mechanism of osmium tetroxide catalysed oxidation of alcohols with alkaline hexacyanoferrate (III) was given by Krishna and Singh⁶⁶. Oxidation kinetics of mandelic acid and olefins was studied by Singh⁶⁷ and coworkers and Mayell⁶⁸ respectively.

Osmium tetroxide catalysed oxidation of maleic acid⁶⁹, glycolate⁷⁰, aldehyde⁷¹, malonate⁷², fumarate⁷³ ions and some diols⁷⁴ have been studied by alkaline hexacyanoferrate (III).

Recently Bharat Singh⁷⁵ and coworkers have reported the oxidation of 2-bromo propionic acid by hexacyanoferrate (III) in presence of osmium tetroxide.

1.2 : PRESENT WORK ON CHLORAMINE - T OXIDATION.

In this section, experimental results on osmium tetroxide catalysed oxidation of p - hydroxy benzoic acid and m -hydroxy benzoic acid by alkaline solution of chloramine - T have been summarised and given below.

- (i) Oxidation of p - hydroxy and m -hydroxy benzoic acids follow first - order kinetics with respect to chloramine-T.
- (ii) Both reactions show first order dependence on each substrates i.e. p -hydroxy benzoic acid and m -hydroxy benzoic acid.
- (iii) The rates of oxidation of p -hydroxy and m -hydroxy benzoic acids were found to show inverse proportionality with sodium hydroxide concentration.
- (iv) Both oxidation processes showed first - order kinetics with respect to osmium tetroxide.
- (v) Effect of variation of ionic strength of the medium, solvent variation and p -toluene sulphonamide concentration effect were negligible in oxidation of both substrates.
- (vi) Temperature variation showed marked effect on the rate of reaction.

(vii) Stoichiometric studies showed that two moles of chloramine - T were required for the oxidation of molar concentration of each substrate. Considering above experimental findings, following rate law was elucidated for the oxidation of p-hydroxy benzoic acid and m-hydroxy benzoic acid (both written as S in rate Law) by chloramine - T (CAT) in alkaline medium using osmium tetroxide as catalyst.

$$\text{Rate} = \frac{2 k_2 k_2^{-1} K [\text{CAT}] [\text{OsO}_4] [\text{S}]}{k_{-2} [\text{NaOH}]} \quad \text{--- (1)}$$

The rate law (1) is in agreement with experimental findings k_2 , k_2^{-1} and k_{-2} are velocity constants of steps of the reaction.

1.3 : PRESNT WORK ON HEXACYANOFERRATE (III) OXIDATION

In this section, the experimental observations recorded in osmium tetroxide catalysed oxidation of 4-butyl morpholine and morpholine butanol by alkaline solution of hexacyanoferrate (iii) have been given in a summarised form.

- (i) The reactions have been found to show zero-order kinetics with respect to hexacyanoferrate (iii).
- (ii) The order of the reaction with respect to each substrate is one.
- (iii) The rates of both reactions have been observed to show direct proportionality with the concentration of the alkali.

- (iv) Oxidation of both the substrates shows first -order dependence on osmium tetroxide.
- (v) Negligible effect of ionic strength variation on reaction rate was observed.
- (vi) The reaction rates are markedly enhanced by rise in temperature.

On the basis of results reported above, the rate law derived is given below :

$$\text{Rate} = n \ k \ K_1 \ K_2 \ [O_s \ O_4] \ [S] \ [OH] \ \text{-----}(2)$$

where n = number of moles of hexacyanoferrate (iii) required to oxidise molar concentration of the substrate, k is velocity constant for rate determining step and K_1, K_2 are equilibrium constants for steps involved in the scheme. Rate law (2) is in complete agreement with experimental observations.

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C H A P T E R - II

M A T E R I A L S A N D E X P E R I M E N T A L

This chapter deals with materials employed and experimental parts that have been used through out the investigation.

2.1 : MATERIALS EMPLOYED

Aqueous solution of chloramine - T was prepared by dissolving an amount of E. Merck, proanalysis sample. The solution was stored in Jena glass bottle coated outside with black Japan to ensure maximum stability.¹ The strength of the solution was checked from time to time by iodometric method.²

Aqueous solutions of p-hydroxy benzoic acid and m-hydroxy benzoic acid of A.R.(B.D.H.) samples were prepared in 50% A.R.(B.D.H.) methanol. Standard solution of sodium hydroxide was obtained by dissolving E. Merck proanalysis sample in boiled double distilled water and was standardised by titrating it against standard solution of oxalic acid using phenolphthalein as indicator.

Standard solution of sodium thiosulphate (Anala R.B.D.H.) was prepared in double distilled water and standardised against standard copper sulphate solution. Aqueous solutions of sodium perchlorate (A.R.Reidel) potassium sulphate (E. Merck, pro analysis) were employed. The p-toluenesulphonamide sample (Koch - light, England) was dissolved in aqueous alkaline double distilled water. A 10% solutions of potassium iodide (A.R.B.D.H.) and 1% starch solution of A.R.(B.D.H.) sample were used.

Osmium tetroxide sample (John Matthey & Co. Limited) was dissolved in aqueous sodium hydroxide and the final strength of osmium tetroxide and sodium hydroxide was kept $15.75 \times 10^{-3} \text{ M}$ and $2 \times 10^{-3} \text{ M}$ respectively.

The samples of 4 - butyl morpholine (L.R.B.D.H.) and morpholine butanol (Fluka grade) were used for investigation without further purification. Their standard solutions were always prepared by dissolving a weighed quantity of the samples in distilled water.

The solution of ceric sulphate was prepared by dissolving a L.R.B.D.H. grade sample in 2 N - sulphuric acid (A.R.B.D.H.) solution. The ceric sulphate solution was standardised against standard solution of ferrous ammonium sulphate G.R. (S. Merck) using ferroin as a redox indicator.

The standard solution of potassium hexacyanoferrate (iii) was prepared by dissolving a calculated amount of G.R. (S. Merck) sample in distilled water.

2.2 : PROCEDURE

The procedures were followed depending upon the nature of the reaction.

A. OXIDATION OF p - HYDROXY AND m - HYDROXY BENZOIC ACIDS BY CHLORAMINE - T.

The reaction mixtures containing requisite amount of substrate alkali and osmium tetroxide were allowed to equilibrate for about half an hour in a water bath maintained at desired

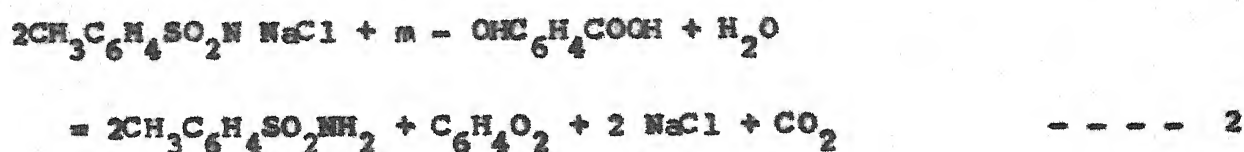
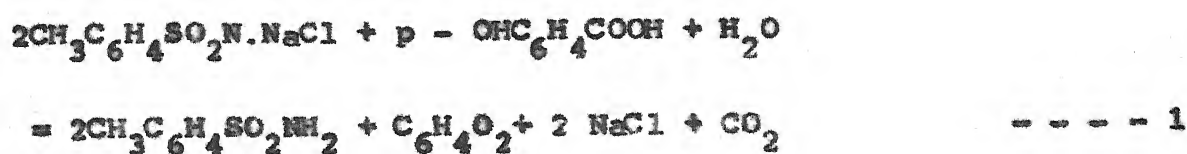
temperature within the range $\pm 0.1^\circ\text{C}$. Appropriate volume of chloramine-T solution maintained separately at same temperature was added to the reaction mixture to initiate the reaction. The progress of the reaction was followed by estimating unconsumed chloramine - T solutions iodometrically in 5 ml aliquot of the reaction mixture taken out at different intervals of time.

B. OXIDATION OF 4-BUTYL MORPHOLINE AND MORPHOLINE BUTANOL BY HEXACYANOFERRATE (III).

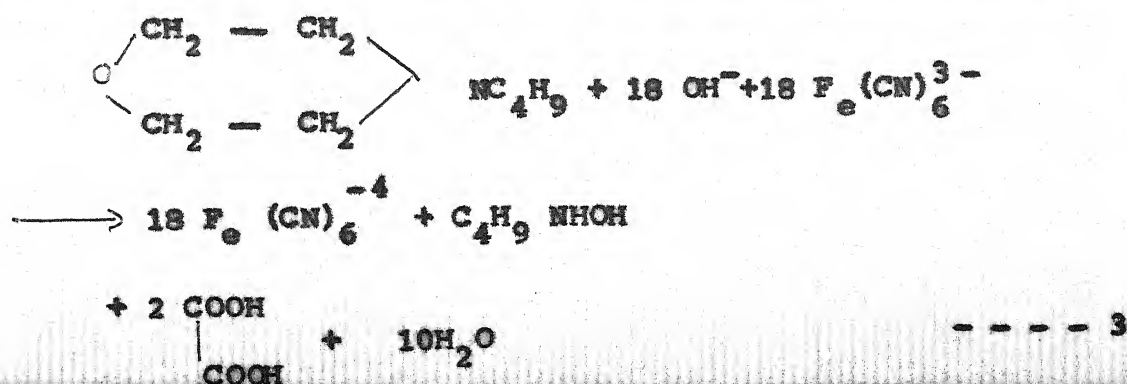
The requisite volumes of standard solutions of potassium hexacyanoferrate (III), sodium hydroxide and osmium tetroxide were taken in a conical stoppered bottle and were maintained in a thermostat with an accuracy of $\pm 0.1^\circ\text{C}$. The solution of organic substrate used was kept in another bottle in the same thermostat when the solutions of both bottles attained the desired temperature, the required volume of the organic substrate was added to the bottle containing other reactants and a stop watch was immediately started to record the time when half the solution in the pipette has passed out in the reaction mixture. The progress of the reaction was observed by estimating an aliquot (5 ml) of the reaction mixture taken out at different intervals of time by a standard solution of ceric sulphate using ferroin as redox indicator. The aliquot of the reaction mixture was first neutralised by 10 ml of 2 N - H_2SO_4 solution to arrest the reaction. The hexacyanoferrate (II) ions produced were estimated by ceric sulphate as stated above.

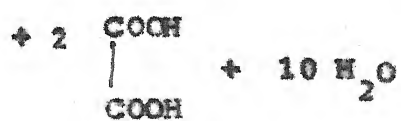
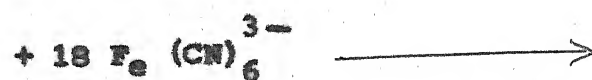
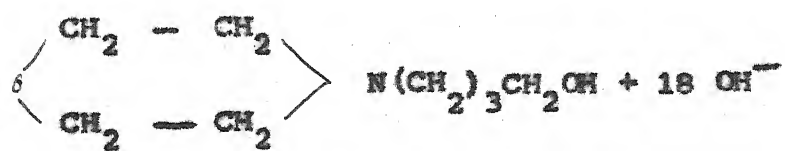
STOICHIOMETRY

Reaction mixture containing a large excess of chloramine - T over the substrate (p-HBA & m-HBA) under the experimental conditions were allowed to stand for 48 hours. The unconsumed chloramine - T was then estimated iodometrically. The experiment showed that two moles of chloramine - T reacted per mole of either p-hydroxy benzoic acid or m-hydroxy benzoic acid and accordingly stoichiometric equations could be represented as given below.



Similarly, in oxidation of morpholine derivatives, the reaction mixture containing a large excess of hexacyanoferrate (iii) over the substrate under the experimental conditions were allowed to stand for 48 hours. The quantity of hexacyanoferrate (ii) ions produced was estimated by ceric sulphate standard solution. The results indicated that 18 moles of hexacyanoferrate (iii) ions were required for oxidation of molar concentration of each compound i.e. 4-butyl morpholine and morpholine butanol. Accordingly, stoichiometric equations may be written as given below.





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C H A P T E R III

KINETICS OF OSMIUM TETROXIDE CATALYSED
OXIDATION OF p - HYDROXY BEN-ZOIC ACID
BY ALKALINE CHLORAMINE - T

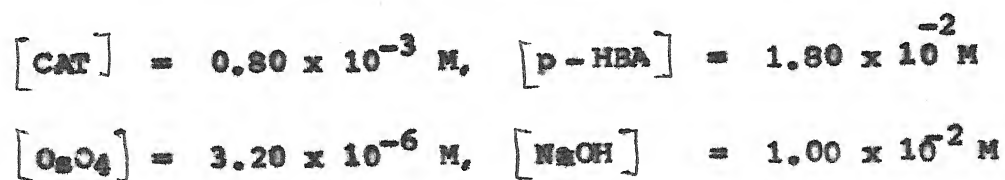
In this chapter an attempt has been made to study the kinetics of oxidation of p-hydroxy benzoic acid by chloramine-T in presence of osmium tetroxide as catalyst. These studies were made in alkaline media and under pseudo-unimolecular conditions by keeping the over all concentration of the reductant comparatively much larger than that of the oxidant stoichiometrically. No buffer could be used during a kinetic run owing to high alkali concentration. This chapter has been divided in many sections. Each section contains experimental results indicating dependence of the reaction on various parameters such as [oxidant], [reducing substance], [catalyst], [alkali], ionic strength of the medium, solvent variation and temperature. For the sake of brevity, chloramine-T, p-toluenesulphonamide and p-hydroxy benzoic acid have been abbreviated as CAT, TSA and p-HBA respectively in the legend of each table giving the experimental data.

3.1 : DEPENDENCE OF THE REACTION ON CHLORAMINE - T CONCENTRATION

In order to determine the dependence of the reaction on oxidant, the reaction was studied at different initial concentrations of chloramine-T keeping the concentration of all other reactants constant. The concentration of chloramine-T was maintained very small as compared to that of p-hydroxy benzoic acid to allow isolation method applicable in calculating the order of the reaction with respect to chloramine-T. The results of these studies are presented in tables 3.1 - 3.6.

TABLE 3.1

Temperature 30°



Time in minute	ml of hypo solution ($2.00 \times 10^{-3} \text{ N}$)	$k_1 \times 10^4 \text{ min}^{-1}$
0	4.00	-
60	3.42	28.02
120	2.86	28.10
180	2.32	27.86
240	1.96	27.98
300	1.60	27.48
360	1.36	28.00
420	1.18	27.60
480	0.96	27.76

Average value of $k_1 = 27.78 \times 10^{-4} \text{ min}^{-1}$

TABLE 3.2

Temperature 30°

$$[\text{CAT}] = 1.00 \times 10^{-3} \text{ M}, \quad [\text{p-HBA}] = 1.80 \times 10^{-2} \text{ M}$$

$$[\text{O}_2\text{O}_4] = 3.20 \times 10^{-6} \text{ M}, \quad [\text{NaOH}] = 1.00 \times 10^{-2} \text{ M}$$

Time in minute	ml of hypo solution ($2.00 \times 10^{-3} \text{ M}$)	$k_1 \times 10^4 \text{ min}^{-1}$
0	5.00	- -
60	4.20	29.08
120	3.54	27.06
180	2.96	27.06
240	2.50	27.08
300	2.10	27.60
360	1.78	27.30
420	1.52	27.28
480	1.26	27.58

Average value of $k_1 = 27.28 \times 10^{-4} \text{ min}^{-1}$

TABLE 3.3

Temperature 30°

$$[\text{CAT}] = 1.20 \times 10^{-3} \text{ M}, \quad [\text{p-HBA}] = 1.80 \times 10^{-2} \text{ M}$$

$$[\text{O}_8\text{C}_4] = 3.20 \times 10^{-6} \text{ M}, \quad [\text{NaOH}] = 1.00 \times 10^{-2} \text{ M}$$

Time in minute	ml of hypo solution ($2.00 \times 10^{-3} \text{ N}$)	$k_1 \times 10^4 \text{ min}^{-1}$
0	6.30	--
60	5.26	28.00
120	4.42	28.06
180	3.70	28.00
240	3.08	27.96
300	2.66	27.46
360	2.18	27.50
420	1.86	28.00
480	1.54	28.56

Average value of $k_1 = 27.94 \times 10^{-4} \text{ min}^{-1}$

TABLE 3.4

Temperature 30°

$$[\text{CAT}] = 1.60 \times 10^{-3} \text{ M}, \quad [\text{p-HBA}] = 1.80 \times 10^{-2} \text{ M}$$

$$[\text{O}_2\text{O}_4] = 3.20 \times 10^{-6} \text{ M}, \quad [\text{NaOH}] = 1.00 \times 10^{-2} \text{ M}$$

Time in minute	ml of hypo solution ($2.00 \times 10^{-3} \text{ M}$)	$k_1 \times 10^4 \text{ min}^{-1}$
0	8.00	--
60	6.62	27.62
120	5.52	27.82
180	4.60	27.48
240	3.92	28.06
300	3.28	28.02
360	2.76	27.56
420	2.30	27.92
480	1.92	28.08

Average value of $k_1 = 27.82 \times 10^{-4} \text{ min}^{-1}$

TABLE 3.5

Temperature 30°

$$[\text{CAT}] = 2.00 \times 10^{-3} \text{M}, \quad [\text{p-HBA}] = 1.90 \times 10^{-2} \text{M}$$

$$[\text{O}_2\text{O}_4] = 3.20 \times 10^{-6} \text{M}, \quad [\text{NaOH}] = 1.00 \times 10^{-2} \text{M}$$

Time in minute	ml of hypo solution ($2.00 \times 10^{-3} \text{N}$)	$k_1 \times 10^4 \text{min}^{-1}$
0	10.00	--
60	8.56	27.86
120	7.26	28.06
180	6.02	27.93
240	5.00	27.58
300	4.18	28.00
360	3.56	27.92
420	2.94	28.02
480	2.48	27.64

Average value of $k_1 = 27.88 \times 10^{-4} \text{min}^{-1}$

TABLE 3.6

Temperature 30°

$$[\text{CAT}] = 2.40 \times 10^{-2} \text{ M}, \quad [\text{p-HBA}] = 1.80 \times 10^{-2} \text{ M}$$

$$[\text{O}_3\text{O}_4] = 3.20 \times 10^{-6} \text{ M}, \quad [\text{NaOH}] = 1.00 \times 10^{-2} \text{ M}$$

Time in minute	ml of hypo solution ($2.00 \times 10^{-3} \text{ N}$)	$k_1 \times 10^4 \text{ min}^{-1}$
0	12.60	--
60	10.50	27.98
120	8.80	28.02
180	7.44	27.68
240	6.20	27.88
300	5.26	28.04
360	4.42	27.46
420	3.72	27.52
480	3.08	27.48

Average value of $k_1 = 27.70 \times 10^{-4} \text{ min}^{-1}$

The results of effect of variation of initial concentration of chloramine - T are summarised in the following table.

TABLE 3.7

Temperature 30°

$$[\text{p - HBA}] = 1.80 \times 10^{-2} \text{ M,}$$

$$[\text{O}_5\text{O}_4] = 3.20 \times 10^{-6} \text{ M, } [\text{NaOH}] = 1.00 \times 10^{-2} \text{ M}$$

$[\text{CAT}] \times 10^3 \text{ M}$	$k_1 \times 10^4 \text{ min}^{-1}$
0.80	27.78
1.00	27.28
1.20	27.94
1.60	27.82
2.00	27.88
2.40	27.70

Average value of $k_1 = 27.74 \times 10^{-4} \text{ min}^{-1}$

It is quite obvious from the results of above table that first - order constant i.e. k_1 values are sensibly constant at all concentrations of chloramine - T. This shows that order of the reaction with respect to chloramine - T is one.

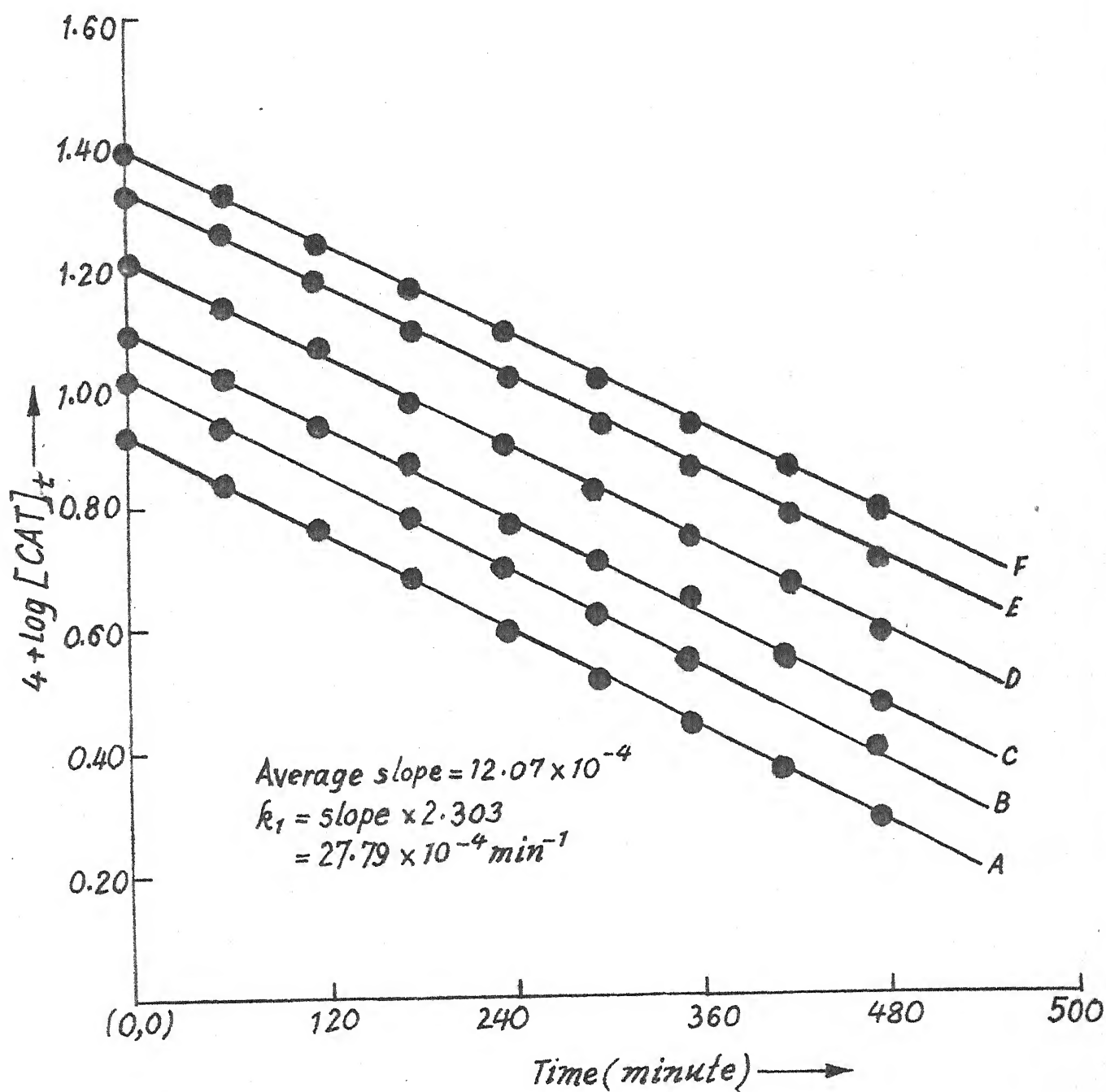


Fig. 3.1 : $[p\text{-HBA}] = 1.80 \times 10^{-2} \text{ M}$, $[O_5O_4] = 3.20 \times 10^{-6} \text{ M}$
 $[\text{NaOH}] = 1.00 \times 10^{-2} \text{ M}$, Temp. 30°C
 $[\text{CAT}] = 0.80 \text{ (A)}, 1.00 \text{ (B)}, 1.20 \text{ (C)}, 1.60 \text{ (D)},$
 $2.00 \text{ (E) and } 2.40 \times 10^{-3} \text{ M (F)}$

In order to confirm the order of the reaction with respect to the oxidant, the value of first-order constant was calculated from the slope of $\log (a - x)$ vs. time plot (Fig.3.1). Average value of k_1 calculated from the slopes of various plots were found to be nearer to that given in table 3.7. This confirms that the reaction follows first - order kinetics with respect to chloramine - T.

3.2 DEPENDENCE OF THE REACTION ON p-HYDROXY BENZOIC ACID CONCENTRATION.

In this section, kinetic studies to investigate the dependence of the reaction rate on the substrate concentration have been made. In order to do so, the rate study measurements were carried out at various initial concentrations of the reductant, keeping the concentration of other reactants fixed. Here also, in each table the concentration of the substrate has been kept much higher than that of chloramine - T. The results are given in the following tables.

TABLE 3.8

Temperature 30°

$$[\text{CAT}] = 1.00 \times 10^{-3} \text{ M}, [\text{p-HBA}] = 1.20 \times 10^{-2} \text{ M}$$

$$[\text{O}_3\text{O}_4] = 3.2 \times 10^{-6} \text{ M}, [\text{NaOH}] = 1.00 \times 10^{-2} \text{ M}$$

Time in minute	ml of hypo solution($2.00 \times 10^{-3}\text{N}$)	$k_1 \times 10^4 \text{ min}^{-1}$
0	5.00	--
60	4.58	19.32
120	4.06	19.20
180	3.72	19.18
240	3.34	19.30
300	2.98	19.24
360	2.64	19.10
420	2.42	19.20
480	2.08	19.22

Average value of $k_1 = 19.22 \times 10^{-4} \text{ min}^{-1}$

TABLE 3.9

Temperature 30°

$$[\text{CAT}] = 1.00 \times 10^{-3} \text{ M}, \quad [\text{p-HBA}] = 1.40 \times 10^{-2} \text{ M}$$

$$[\text{O}_5\text{O}_4] = 3.20 \times 10^{-6} \text{ M}, \quad [\text{NaOH}] = 1.00 \times 10^{-2} \text{ M}$$

Time in minute	ml of hypo solution ($2.00 \times 10^{-3} \text{ N}$)	$k_1 \times 10^4 \text{ min}^{-1}$
0	5.00	--
60	4.40	22.60
120	3.82	22.92
180	3.32	22.88
240	2.90	22.76
300	2.54	22.96
360	2.22	22.98
420	1.92	22.86
480	1.68	23.00

Average value of $k_1 = 22.87 \times 10^{-4} \text{ min}^{-1}$

TABLE 3.10

Temperature 30°

$$[\text{CAT}] = 1.00 \times 10^{-3} \text{ M}, \quad [\text{p-HBA}] = 1.80 \times 10^{-2} \text{ M}$$

$$[\text{O}_8\text{O}_4] = 3.20 \times 10^{-6} \text{ M}, \quad [\text{NaOH}] = 1.00 \times 10^{-2} \text{ M}$$

Time in minute	ml of hypo solution ($2.00 \times 10^{-3} \text{ N}$)	$k_1 \times 10^4 \text{ min}^{-1}$
0	5.00	--
60	4.18	29.08
120	3.56	29.06
180	2.98	29.30
240	2.50	29.08
300	2.08	27.60
360	1.76	29.32
420	1.50	29.28
480	1.24	29.58

Average value of $k_1 = 29.32 \times 10^{-4} \text{ min}^{-1}$

TABLE 3.11

Temperature 30°

$$[\text{CAT}] = 1.00 \times 10^{-3} \text{ M}, \quad [\text{p-HEA}] = 2.25 \times 10^{-2} \text{ M}$$

$$[\text{O}_3\text{O}_4] = 3.20 \times 10^{-6} \text{ M}, \quad [\text{NaOH}] = 1.00 \times 10^{-2} \text{ M}$$

Time in minute	ml of hypo solution ($2.00 \times 10^{-3} \text{ N}$)	$k_1 \times 10^4 \text{ min}^{-1}$
0	5.00	--
60	3.98	37.14
120	3.14	38.74
180	2.48	38.88
240	1.92	39.00
300	1.50	40.00
360	1.20	39.44
420	0.98	38.76
480	0.74	39.75

Average value of $k_1 = 38.96 \times 10^{-4} \text{ min}^{-1}$

TABLE 3.12

Temperature 30°

$$[\text{CAT}] = 1.00 \times 10^{-3} \text{ M}, \quad [\text{p-HBA}] = 3.00 \times 10^{-2} \text{ M}$$

$$[\text{O}_8\text{O}_4] = 3.20 \times 10^{-6} \text{ M}, \quad [\text{NaOH}] = 1.00 \times 10^{-2} \text{ M}$$

Time in minute	ml of hypo solution ($2.00 \times 10^{-3}\text{N}$)	$k_1 \times 10^4 \text{min}^{-1}$
0	5.00	--
30	4.18	54.06
60	3.54	53.92
90	2.96	55.00
120	2.50	54.20
150	2.08	54.18
180	1.80	54.00
210	1.44	54.08
240	1.24	53.98

Average value of $k_1 = 54.18 \times 10^{-4} \text{min}^{-1}$

The results of tables 3.8 - 3.12 are summarised in the following table.

TABLE 3.13

$$[\text{CAT}] = 1.00 \times 10^{-3} \text{ M}, \quad [\text{O}_2\text{O}_4] = 3.20 \times 10^{-2} \text{ M}$$

$$[\text{NaOH}] = 1.00 \times 10^{-2} \text{ M}, \quad \text{Temperature } 30^\circ$$

$[\text{p-HBA}] \times 10^2$ M	$k_1 10^4$ min^{-1}	$k_2 10^2 = \frac{k_1}{[\text{p-HBA}]}$ $\text{mol}^{-1} \text{ l min}^{-1}$
1.20	19.22	16.02
1.40	22.87	16.34
1.80	29.32	16.28
2.25	38.96	17.31
3.00	54.18	18.06

A careful perusal of above data indicates that first - order rate constant (k_1) values increase linearly with the increase in the initial concentration of p-hydroxy benzoic acid and second order rate constant (k_2) values ($k_1 / [\text{p-HBA}]$) are fairly constant at all initial concentrations of p-hydroxy benzoic acid. This shows that the reaction follows first order

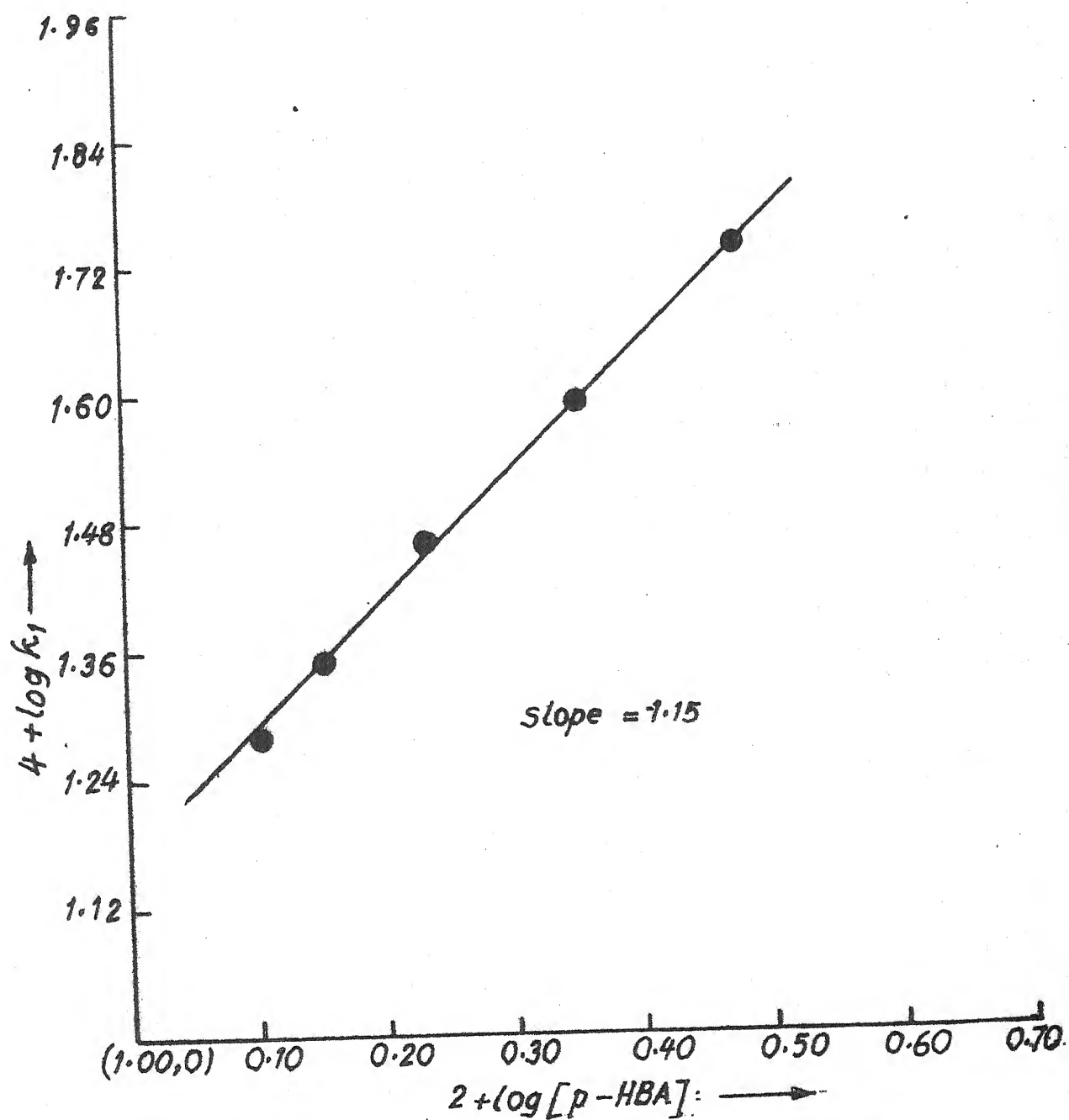


Fig. 3.2 : $[CAT] = 1.00 \times 10^{-3} M$, $[OsO_4] = 3.20 \times 10^{-6} M$
 $[NaOH] = 1.00 \times 10^{-2} M$, Temp. $30^\circ C$

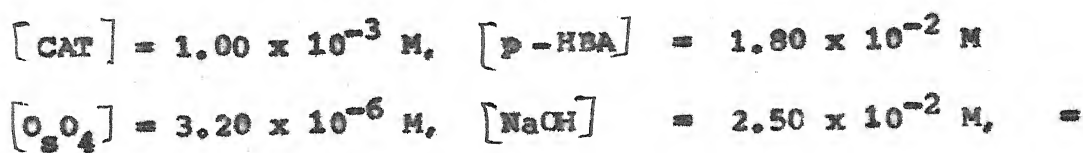
kinetics in the substrate. This observation is, further, confirmed by $\log k_1 - \log [p\text{-HBA}]$ plot (Fig.322) which gives a straight line whose slope is equal to 1.15 showing and confirming thereby first - order dependence of the reaction on p - hydroxy benzoic acid.

3.3 DEPENDENCE OF THE REACTION ON ALKALI CONCENTRATION

The reaction was found to be highly influenced by alkali concentration variation. To investigate the dependence of oxidation of p - hydroxy benzoic acid by O_3 (VIII) catalysis in presence of chloramine - T as oxidant on alkali concentration, a series of experiments was performed at different initial concentrations of alkali and keeping the concentrations of all other reactants at constant level. In order to annul the effect of ionic strength of the medium, if any, by varying alkali concentration, suitable amounts of sodium perchlorate were added to the reaction mixture to maintain the ionic strength of the medium constant in all experiments in this section. The results are given in the following tables.

TABLE 3.14

Temperature 30°



Time in minute	ml of hypo solution ($2.00 \times 10^{-3} \text{ N}$)	$k_1 \times 10^4 \text{ min}^{-1}$
0	5.00	- -
60	4.66	11.73
120	4.34	11.81
180	4.08	11.28
240	3.76	11.77
300	3.50	11.87
360	3.22	12.20
420	3.00	12.15
480	2.82	11.92

Average value of $k_1 = 11.84 \times 10^{-4} \text{ min}^{-1}$

TABLE 3.15

Temperature 30°

[CAT] = 1.00×10^{-3} M, [p-HBA] = 1.80×10^{-2} M[O₂O₄] = 3.20×10^{-6} M, [NaOH] = 1.50×10^{-2} M, =

Time in minute	ml of hypo solution (2.00×10^{-3} N)	$k_1 \times 10^4 \text{ min}^{-1}$
0	5.00	- -
60	4.50	17.56
120	4.00	18.57
180	3.52	19.48
240	3.18	19.00
300	2.90	18.88
360	2.60	19.12
420	2.30	18.45
480	2.04	18.70

Average value of $k_1 = 18.72 \times 10^{-4} \text{ min}^{-1}$

TABLE 3.16

Temperature 30°

 $[CAT] = 1.00 \times 10^{-3} \text{ M}, [p-HBA] = 1.80 \times 10^{-2} \text{ M}$
 $[O_3O_4] = 3.20 \times 10^{-6} \text{ M}, [NaOH] = 1.00 \times 10^{-2} \text{ M}, =$

Time in minute	ml of hypo solution ($2.00 \times 10^{-3} \text{ N}$)	$k_1 \times 10^4 \text{ min}^{-1}$
0	5.00	--
60	4.20	29.06
120	3.56	28.21
180	2.96	28.53
240	2.50	29.00
300	2.08	29.20
360	1.78	28.10
420	1.50	28.61
480	1.24	29.00

Average value of $k_1 = 28.71 \times 10^{-4} \text{ min}^{-1}$

TABLE 3.17

Temperature 30°

$$[\text{CAT}] = 1.00 \times 10^{-2} \text{ M}, \quad [\text{p-HBA}] = 1.80 \times 10^{-2} \text{ M}$$

$$[\text{O}_2\text{O}_4] = 3.20 \times 10^{-6} \text{ M}, \quad [\text{NaOH}] = 0.85 \times 10^{-2} \text{ M}, \quad =$$

Time in minute	ml of hypo solution ($2.00 \times 10^{-3} \text{ N}$)	$k_1 \times 10^4 \text{ min}^{-1}$
0	5.00	--
60	4.00	37.14
120	3.18	37.68
180	2.62	36.00
240	2.12	35.71
300	1.76	35.00
360	1.42	34.64
420	1.12	35.00
480	0.94	34.80

Average value of $k_1 = 35.75 \times 10^{-4} \text{ min}^{-1}$

TABLE 3.18

Temperature 30°

$$[\text{CAT}] = 1.00 \times 10^{-3} \text{ M}, \quad [\text{p-HBA}] = 1.80 \times 10^{-2} \text{ M}$$

$$[\text{O}_3\text{O}_4] = 3.20 \times 10^{-6} \text{ M}, \quad [\text{NaOH}] = 0.60 \times 10^{-2} \text{ M}$$

Table in minute	ml of hypo solution ($2.00 \times 10^{-3} \text{ N}$)	$k_1 \times 10^4 \text{ min}^{-1}$
0	5.00	--
60	3.74	48.34
120	2.82	47.68
180	2.14	47.09
240	1.68	45.23
300	1.28	45.37
360	0.98	45.22
420	0.80	45.58

Average value of $k_1 = 46.07 \times 10^{-4} \text{ min}^{-1}$

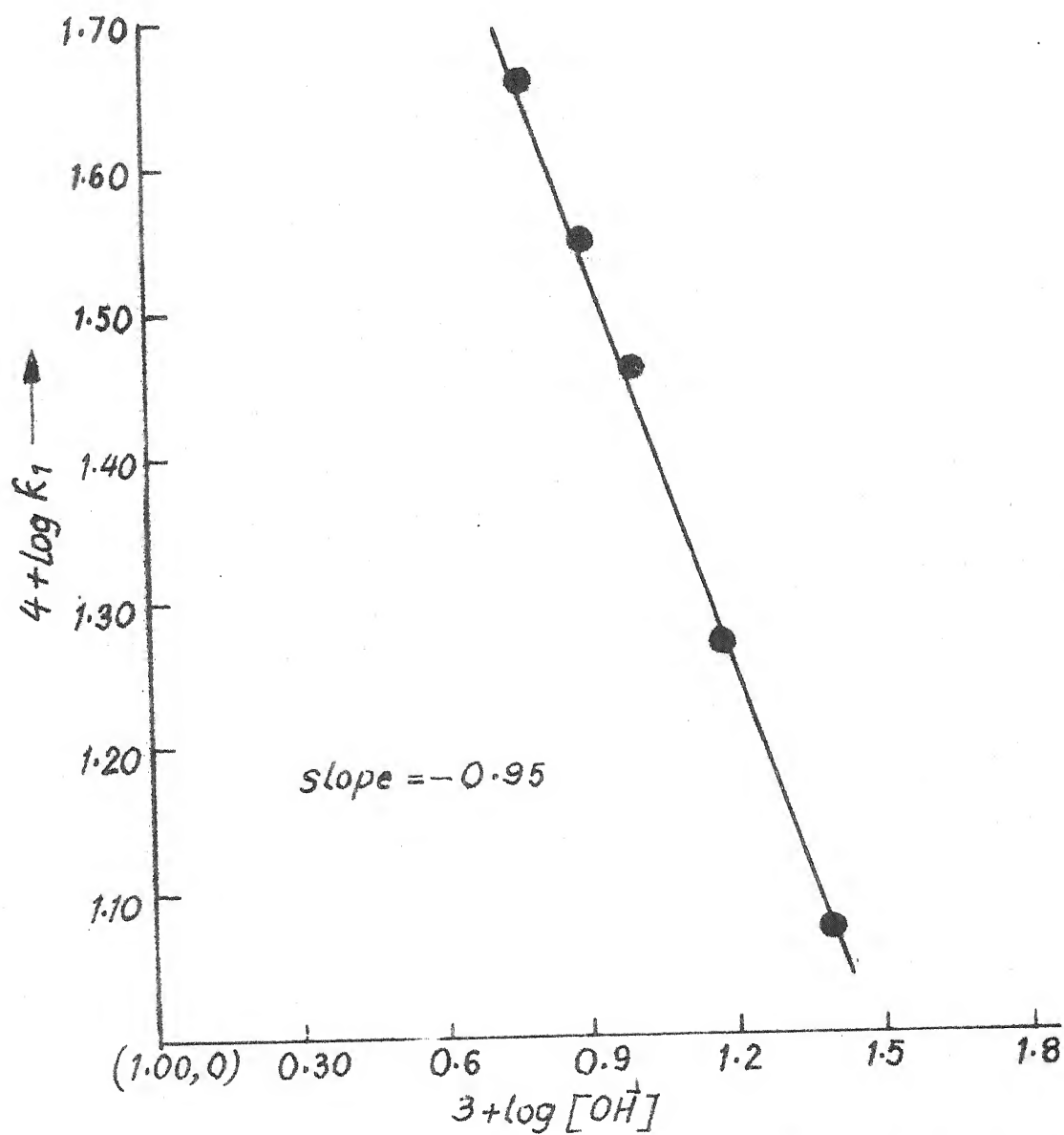


Fig. 3.3 : $[\text{CAT}] = 1.00 \times 10^{-3} \text{M}$, $[\text{p-HBA}] = 1.80 \times 10^{-2} \text{M}$
 $[\text{O}_5\text{O}_4] = 3.20 \times 10^{-6} \text{M}$, Temp. 30°

The results of tables 3.14 - 3.18 are summarised below.

TABLE 3.19

Temperature 30°

$$[\text{CAT}] = 1.00 \times 10^{-3} \text{ M}, \quad [\text{p-HBA}] = 1.80 \times 10^{-2} \text{ M}$$

$$[\text{O}_2\text{O}_4] = 3.20 \times 10^6 \text{ M},$$

$[\text{NaOH}] \times 10^2$ M	$k_1 \times 10^4$ min^{-1}	$k_2 \times 10^2$ $\text{mol}^{-1} \text{ l min}^{-1}$
2.50	11.84	8.16
1.50	18.72	15.60
1.00	28.71	28.71
0.85	35.75	42.05
0.60	46.07	65.72

A perusal of above table indicates that on increasing the alkali concentration the value of first - order rate constant (i.e. k_1) decreases. Also the value of k_2 (second order constant = $k_1 / [\text{OH}^-]$) decreases with the increase in alkali. Thus the first - order rate constant with respect to alkali is ruled out. For determining the dependence of the reaction on alkali, a graph between $\log k_1$ and $\log [\text{OH}^-]$ was plotted (Fig. 3.3). A straight line with a slope of -0.9 has been obtained, which shows that order of the reaction with respect to alkali is nearly minus one (-1).

3.4 DEPENDENCE OF THE REACTION ON OSMIUM TETROXIDE CONCENTRATION

In this section, an attempt has been made to determine the order of the reaction with respect to osmium tetroxide. In order to do so, various experiments were performed at various initial concentrations of osmium tetroxide but at fixed concentration of all the remaining reactants. It was observed that first - order constant (i.e. k_1) value increases with the increase in osmium tetroxide concentration. The summarised results are given in the following table.

TABLE 3.20

Temperature 30°

$$[\text{CAT}] = 2.00 \times 10^{-3} \text{ M}, \quad [\text{p-HBA}] = 1.80 \times 10^{-2} \text{ M}$$

$$[\text{NaOH}] = 1.00 \times 10^{-2} \text{ M}, \quad \mu = 0.20 \text{ M}$$

(adjusted by addition of NaClO_4 solution)

$[\text{OsO}_4] \times 10^6 \text{ M}$	$k_1 \times 10^3 \text{ min}^{-1}$	$k_2 \times 10^{-2} \text{ mole}^{-1} \text{ l min}^{-1}$
0.80	0.70	8.75
1.60	1.42	8.87
2.40	2.14	8.91
3.20	2.80	8.75
4.00	3.54	8.85
4.80	4.22	8.79

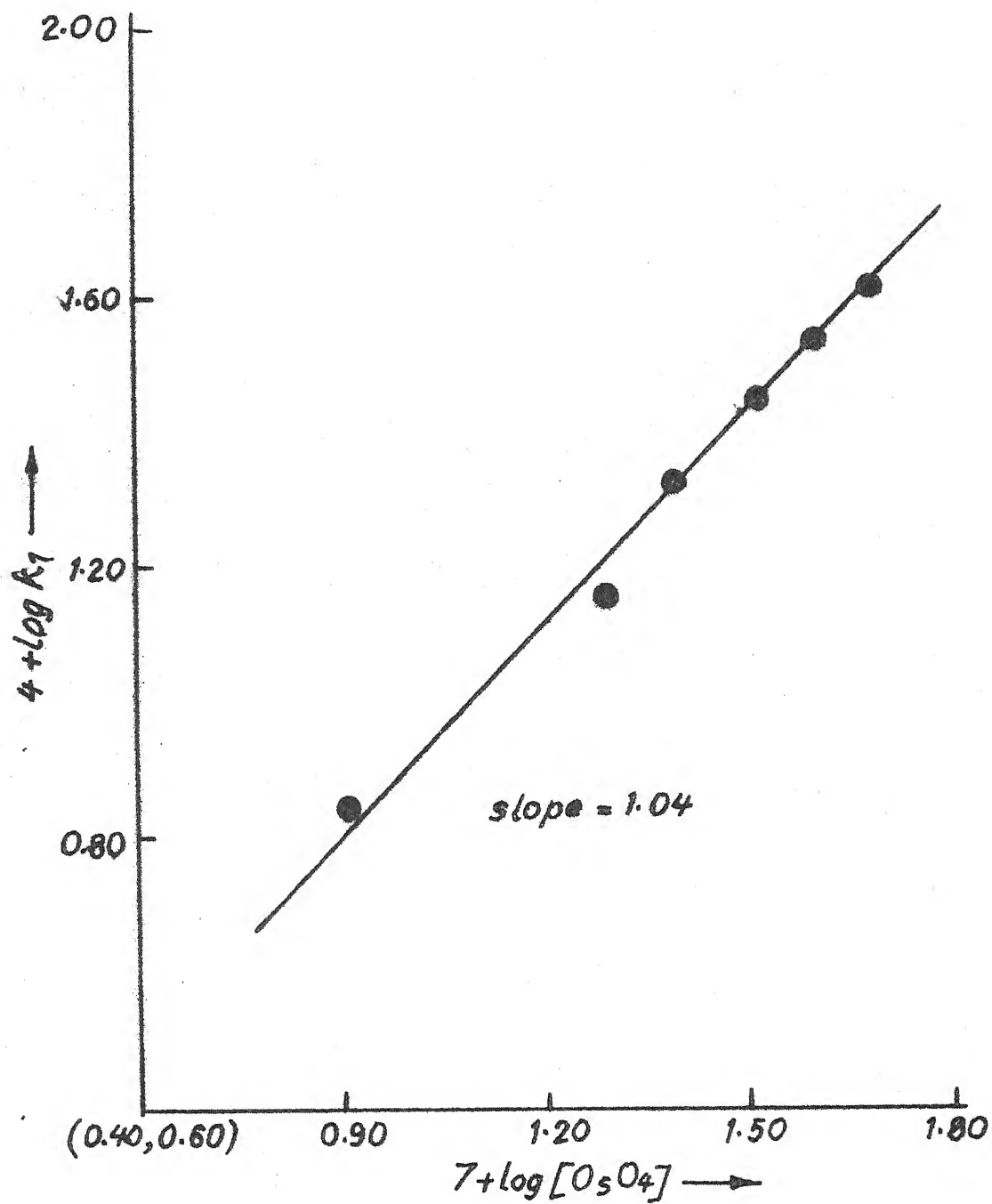


Fig. 3.4: $[CAT] = 1.00 \times 10^{-3} M$, $[p-HBA] = 1.80 \times 10^{-2} M$,
 $[NaOH] = 1.00 \times 10^{-2} M$, Temp. 30°

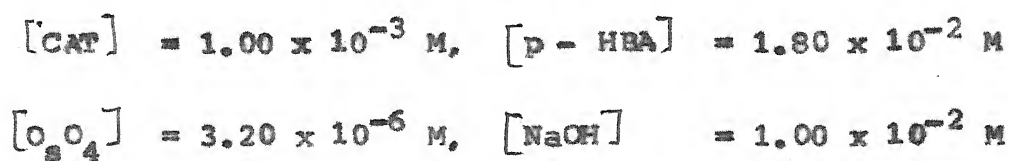
A perusal of 3rd column of above table shows the constancy of k_2 (second order constant) values which indicates first - order dependence of the reaction rate on osmium tetroxide concentration. A graph between $\log [\text{OsO}_4]$ and $\log k_1$ also yields a straight line (Fig. 3.4) with a slope equal to 1.04 which confirms that order of the reaction with respect to osmium tetroxide is one.

3.5 DEPENDENCE OF IONIC STRENGTH ON REACTION RATE

In this section, the results of effect of ionic strength variation (by using sodium perchlorate and potassium sulphate solution) on reaction rate have been reported.

TABLE 3.21

Temperature 30°



$[\text{NaClO}_4] \text{ M}$	$\mu(\text{M})$	$k_1 \times 10^{-4} \text{ min}^{-1}$	$[\text{K}_2\text{SO}_4] \text{ M}$	$\mu(\text{M})$	$k_2 \times 10^4 \text{ min}^{-1}$
0.0	0.01	28.20	0.0	0.01	28.20
0.2	0.21	28.10	0.1	0.11	28.12
0.4	0.41	28.12	0.3	0.31	28.10
0.6	0.61	28.04	0.5	0.51	28.14
0.8	0.81	28.02	0.7	0.71	28.12

It is clear from the data of above table that the reaction rate remains unaffected by change in the ionic strength of the medium.

3.6 DEPENDENCE OF THE REACTION RATE ON SOLVENT COMPOSITION

Kinetic results obtained in water - methanol mixtures of different compositions and at fixed concentrations of other reactants are given in the following table.

TABLE 3.22

$$\begin{aligned}
 [\text{CAT}] &= 1.00 \times 10^{-3} \text{ M}, & [\text{p-HBA}] &= 1.80 \times 10^{-2} \text{ M} \\
 [\text{O}_8\text{O}_4] &= 3.20 \times 10^{-6} \text{ M}, & [\text{NaOH}] &= 1.00 \times 10^{-2} \text{ M}
 \end{aligned}$$

Me OH % (V/V)	$k_1 \times 10^4 \text{ min}^{-1}$
00	28.00
10	28.12
20	28.10
30	28.06
40	28.14

An examination of data of above table shows insignificant effect of change in the solvent composition on reaction rate.

3.7 DEPENDENCE OF RATE ON p - TOLUENE SULPHONAMIDE CONCENTRATION

In order to see the effect of p-toluene sulphonamide (one of the reaction products) on the reaction rate, kinetics runs were taken at various initial concentrations of TSA and results are summarised in table 3.23.

$$[\text{CAT}] = 1.00 \times 10^{-3} \text{ M}, \quad [\text{p - MBA}] = 1.80 \times 10^{-2} \text{ M}$$

$$[\text{OsO}_4] = 3.20 \times 10^{-6} \text{ M}, \quad [\text{NaOH}] = 1.00 \times 10^{-2} \text{ M}$$

$[\text{TSA}] \times 10^3 \text{ M}$	$k_1 \times 10^4 \text{ min}^{-1}$
0.00	28.02
0.25	28.04
0.50	28.10
0.75	28.06
1.00	28.02
1.50	28.10
2.00	28.08

It is quite obvious from the results of above table that the variation of p-toluene sulphonamide concentration does not alter the reaction rate for the oxidation of p-hydroxy benzoic acid by alkaline chloramine - T solution in presence of osmium tetroxide as catalyst.

3.8 DEPENDENCE OF THE REACTION RATE ON TEMPERATURE

This section deals with the effect of temperature variation on the reaction rate. Experiments at constant concentrations of all reactants have been performed at 25, 30, 35 and 40°C. Result at 30°C has already been reported. The following tables present the kinetic data at 25, 35 and 40°C. These data have been utilised in calculating the values of energy of activation, and entropy of activation.

TABLE 3.24

Temperature 25°C

$$[\text{CAT}] = 1.00 \times 10^{-3} \text{ M}, [\text{p-HBA}] = 1.80 \times 10^{-2} \text{ M}$$

$$[\text{O}_5\text{O}_4] = 3.20 \times 10^{-6} \text{ M}, [\text{NaOH}] = 1.00 \times 10^{-2} \text{ M}$$

Time in minute	ml of hypo solution ($2.00 \times 10^{-3} \text{ N}$)	$k_1 \times 10^4 \text{ min}^{-1}$
0	5.00	--
60	4.42	20.54
120	3.86	21.54
180	3.38	21.73
240	2.90	22.67
300	2.52	22.00
360	2.18	22.52
420	1.88	24.90
480	1.62	23.45

Average value of $k_1 = 22.42 \times 10^{-4} \text{ min}^{-1}$

TABLE 3.25

Temperature 35°

$$[\text{CAT}] = 1.00 \times 10^{-3} \text{ M}, \quad [\text{p-HBA}] = 1.80 \times 10^{-2} \text{ M}$$

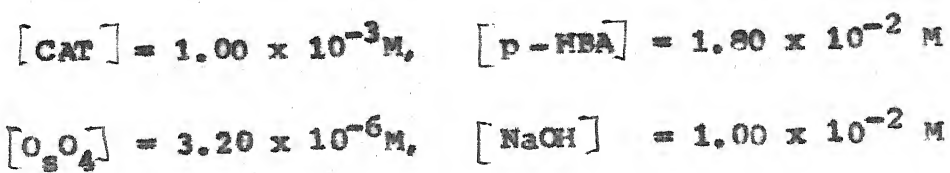
$$[\text{O}_5\text{O}_4] = 3.20 \times 10^{-6} \text{ M}, \quad [\text{NaOH}] = 1.00 \times 10^{-2} \text{ M}$$

Time in minute	ml of hypo solution ($2.00 \times 10^{-3} \text{ N}$)	$k_1 \times 10^4 \text{ min}^{-1}$
0	5.00	--
60	4.00	37.14
120	3.22	37.52
180	2.60	35.96
240	2.08	36.00
300	1.70	35.48
360	1.32	35.24
420	1.10	35.12
480	0.96	34.96

Average value of $k_1 = 35.92 \times 10^{-4} \text{ min}^{-1}$

TABLE 3.26

Temperature 40°



Time in minute	ml of hypo solution($2.00 \times 10^{-3}\text{N}$)	$k_1 \times 10^4 \text{min}^{-1}$
0	5.00	--
40	4.12	48.36
80	3.38	48.90
120	2.80	48.26
160	2.36	46.88
210	1.86	47.00
250	1.60	45.53
300	1.20	47.51

Average value of $k_1 = 47.49 \times 10^{-4} \text{min}^{-1}$

The results of tables 3.34 - 3.26 and table 3.2 have been summarised in table 3.27.

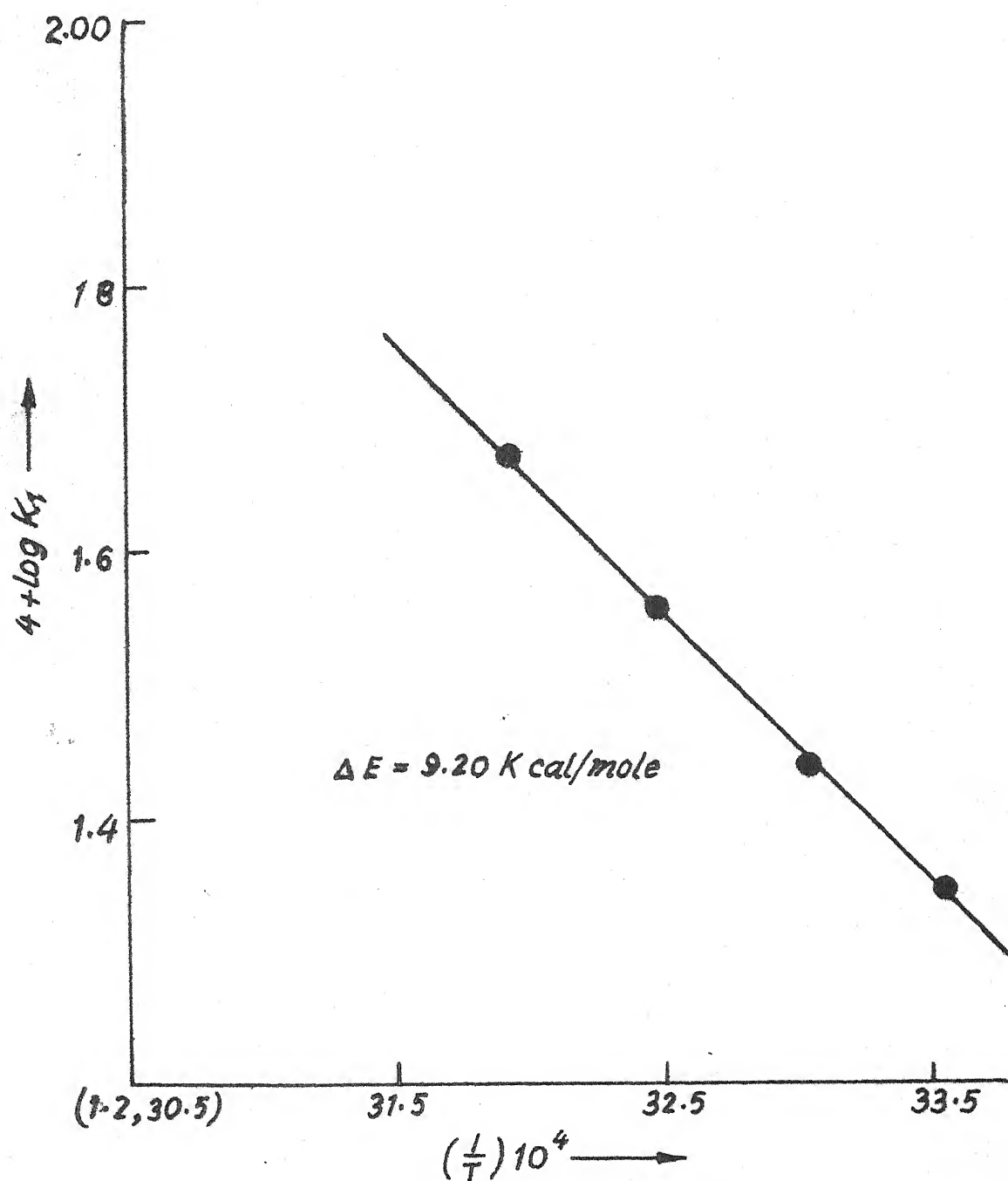


Fig. 3.5: $[\text{CAT}] = 1.00 \times 10^{-3} \text{ M}$, $[\text{p-HBA}] = 1.80 \times 10^{-2} \text{ M}$
 $[\text{O}_5\text{O}_4] = 3.20 \times 10^{-6} \text{ M}$, $[\text{NaOH}] = 1.00 \times 10^{-2} \text{ M}$

TABLE 3.27

$$[\text{CAT}] = 1.00 \times 10^{-3} \text{ M}, \quad [\text{p-HBA}] = 1.80 \times 10^{-2} \text{ M}$$

$$[\text{O}_2\text{O}_4] = 3.20 \times 10^{-6} \text{ M} \quad \text{and} \quad [\text{NaOH}] = 1.00 \times 10^{-2} \text{ M}$$

Temperature °C	$k_1 \times 10^4 \text{ min}^{-1}$
25	22.42
30	27.28
35	35.92
40	47.49

In order to calculate the value of energy of activation i.e. ΔE , a graph between $\log k$ and $\frac{1}{T}$ was plotted. The slope of the curve (Fig. 3.5) gave the value of $\Delta E/2.303R$ according to Arrhenius equation

$$\log k = \log A - \frac{\Delta E}{2.303 RT}$$

The value of ΔE thus calculated was found to be 9.20 K cal/mole.

C H A P T E R I V

KINETICS OF OSMIUM TETROXIDE CATALYSED
OXIDATION OF m - HYDROXY BENZOIC ACID
BY ALKALINE CHLORAMINE - T

This chapter deals with the experiments performed to determine the order of the reaction between alkaline solution of chloramine - T and m - hydroxy benzoic acid in the presence of osmium tetroxide as catalyst with respect to the oxidant, reducing substance, alkali and osmium tetroxide. In addition, an attempt has also been made to investigate the effects of ionic strength of the media, solvent variation, p - toluene sulphonamide (one of the reaction products) and temperature variation. The chapter has been divided in many sections. Each section deals with series of experiments performed to determine either the kinetic order with respect to one reactant or to investigate the effect of one parameter described above. Here also, for the sake of brevity chloramine - T, p - toluene sulphonamide and m - hydroxy benzoic acid have been abbreviated as CAT, TSA and m - HBA respectively in the legend of each table.

4.1 DETERMINATION OF ORDER OF THE REACTION WITH RESPECT TO CHLORAMINE - T CONCENTRATION

In this section an attempt has been made to determine the dependence of the reaction on oxidant. In order to do so, various experiments at different concentrations of chloramine-T but at fixed concentrations of all other reactants have been performed at 30°C. The results obtained are tabulated in the following tables. All experiments have been performed without keeping ionic strength constant as preliminary studies showed its negligible effect.

TABLE 4.1

Temperature 30°

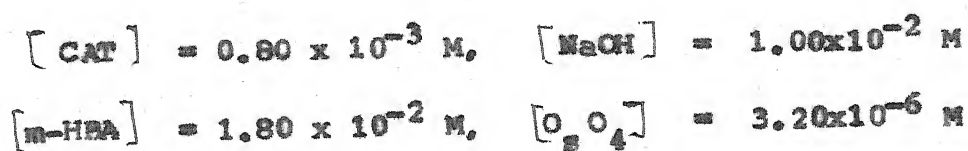
$$[\text{CAT}] = 0.80 \times 10^{-3} \text{ M}, \quad [\text{NaOH}] = 1.00 \times 10^{-2} \text{ M}$$

$$[\text{m-HBA}] = 1.80 \times 10^{-2} \text{ M}, \quad [\text{O}_3\text{O}_4] = 3.20 \times 10^{-6} \text{ M}$$

Time (minutes)	ml of hypo solution ($2.00 \times 10^{-3} \text{ N}$)	$k_1 \times 10^4 \text{ min}^{-1}$
0	4.00	--
60	3.42	26.10
120	2.88	27.35
180	2.46	26.98
240	2.08	26.99
300	1.80	26.59
360	1.56	26.13
420	1.32	26.36
480	1.10	27.00

TABLE 4.2

Temperature 30°



Time (minutes)	ml of hypo solution ($2.00 \times 10^{-3} \text{N}$)	$k_1 \times 10^4 \text{min}^{-1}$
0	5.00	--
60	4.28	25.92
120	3.64	26.43
180	3.08	26.88
240	2.60	27.20
300	2.26	26.44
360	1.92	26.55
420	1.64	26.52
480	1.36	27.10

Average value of $k_1 = 26.63 \times 10^{-4} \text{min}^{-1}$

TABLE 4.3

Temperature 30°

$$[\text{CAT}] = 1.20 \times 10^{-3} \text{ M}, \quad [\text{NaOH}] = 1.00 \times 10^{-2} \text{ M}$$

$$[\text{m-HBA}] = 1.80 \times 10^{-2} \text{ M}, \quad [\text{O}_5\text{O}_4] = 3.20 \times 10^{-6} \text{ M}$$

Time (minutes)	ml of hypo solution ($2.00 \times 10^{-3} \text{ N}$)	$k_1 \times 10^4 \text{ min}^{-1}$
0	6.32	--
60	5.36	27.10
120	4.52	29.91
180	3.88	27.08
240	3.26	27.00
300	2.80	27.09
360	2.40	26.86
420	2.00	27.36
480	1.72	27.08

Average value of $k_1 = 27.18 \times 10^{-4} \text{ min}^{-1}$

TABLE 4.4

Temperature 30°

$$[\text{CAT}] = 1.60 \times 10^{-3} \text{ M}, [\text{NaOH}] = 1.00 \times 10^{-2} \text{ M}$$

$$[\text{m-HBA}] = 1.80 \times 10^{-2} \text{ M}, [\text{O}_8\text{O}_4] = 3.20 \times 10^{-6} \text{ M}$$

Time (minutes)	ml of hypo solution ($2.00 \times 10^{-3}\text{N}$)	$k_1 \times 10^4 \text{ min}^{-1}$
0	7.92	--
60	6.60	26.34
120	5.60	27.34
180	4.82	26.98
240	4.08	26.92
300	3.48	26.80
360	2.94	26.43
420	2.50	26.80
480	2.08	27.18

Average value of $k_1 = 26.85 \times 10^{-4} \text{ min}^{-1}$

TABLE 4.5

Temperature 30°

$$[\text{CAT}] = 2.00 \times 10^{-3} \text{ M}, \quad [\text{NaOH}] = 1.00 \times 10^{-2} \text{ M}$$

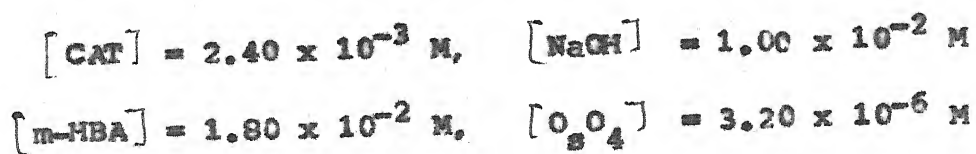
$$[\text{m-HBA}] = 1.80 \times 10^{-2} \text{ M}, \quad [\text{O}_2\text{O}_4] = 3.20 \times 10^{-6} \text{ M}$$

Time (minutes)	ml of hypo solution ($2.00 \times 10^{-3} \text{ M}$)	$k_1 \times 10^4 \text{ min}^{-1}$
0	10.00	--
50	8.78	25.99
120	7.42	25.00
180	6.10	26.86
240	5.20	27.20
300	4.52	26.44
360	3.80	26.56
420	3.14	26.72
480	2.70	27.20

Average value of $k_1 = 26.50 \times 10^{-4} \text{ min}^{-1}$

TABLE 4.6

Temperature 30°



Time (minutes)	ml of hypo solution ($2.00 \times 10^{-3} \text{ N}$)	$k_1 \times 10^4 \text{ min}^{-1}$
0	12.60	--
60	10.72	27.12
120	9.04	27.91
180	7.76	27.08
240	6.50	27.02
300	5.62	27.08
360	4.80	26.86
420	4.00	27.36
480	3.42	27.06

Average value of $k_1 = 27.18 \times 10^{-4} \text{ min}^{-1}$

The results of above table are summarised in Table 4.7.

TABLE 4.7

$$[m - HBA] = 1.80 \times 10^{-2} \text{ M}, [NaOH] = 1.00 \times 10^{-2} \text{ M}$$

$$[O_3, O_4] = 3.20 \times 10^{-6} \text{ M}, \text{ Temperature } 30^\circ$$

$[CAT] \times 10^3 \text{ M}$	$k_1 \times 10^4 \text{ min}^{-1}$
0.80	26.70
1.00	26.63
1.20	27.18
1.60	26.85
2.00	26.50
2.40	27.38

Average value of $k_1 = 26.84$

It is evident from the values of k_1 first - order rate constant given in 2nd column of above table that at all concentrations of chloramine - T the values of k_1 do not change appreciably and are quite nearer to each other showing thereby, first order kinetics in chloramine - T.

In order to, further, confirm the dependence of the reaction on chloramine - T, a plot of $\log (a/a-x)$ vs. time was drawn (Table 4.1). A straight line passing through origin (Fig.4.1) was obtained. The slope of the curve gave

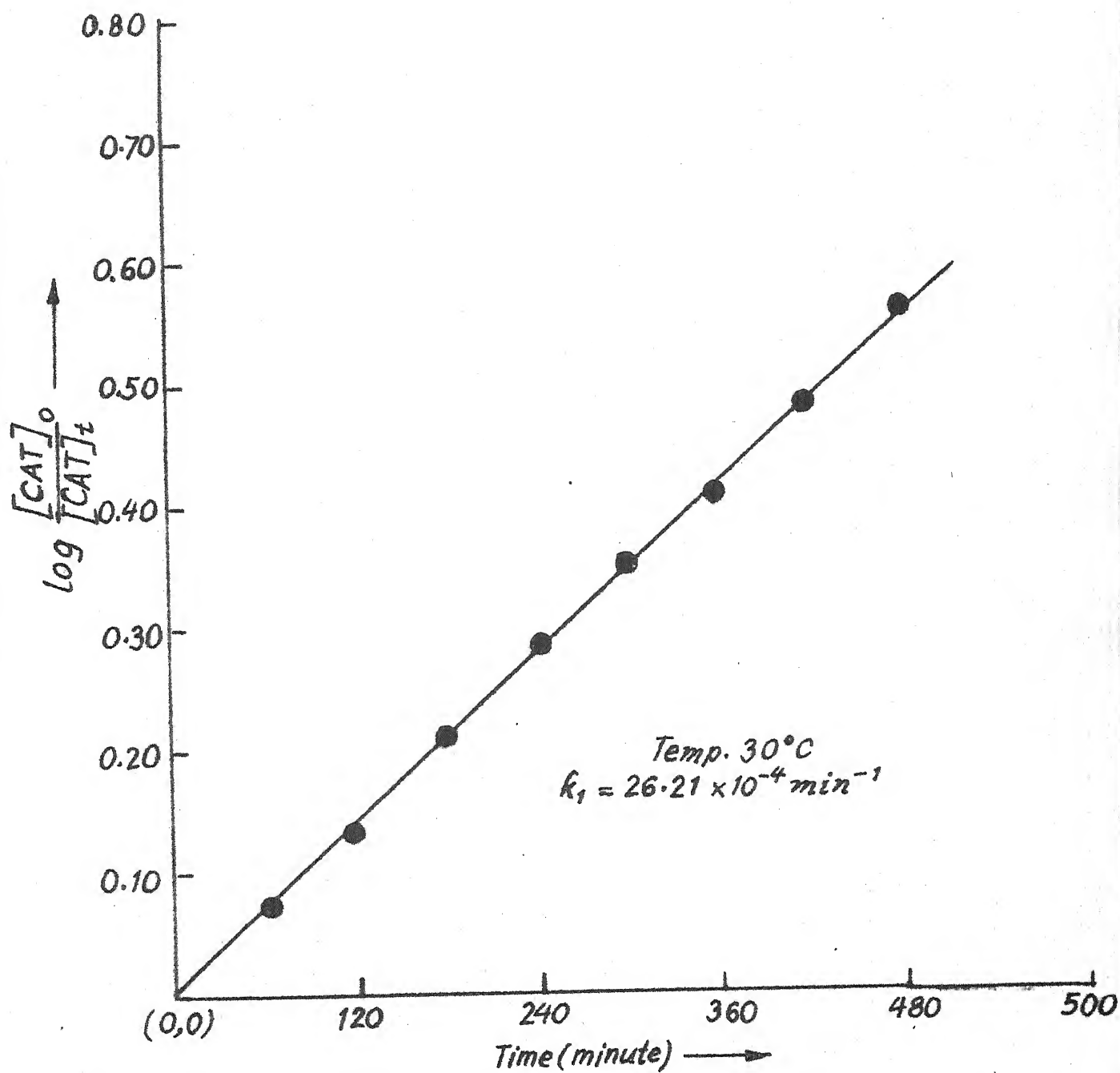


Fig. 4.1 : $[\text{CAT}] = 0.80 \times 10^{-3} \text{ M}$, $[\text{NaOH}] = 1.00 \times 10^{-2} \text{ M}$
 $[\text{OsO}_4] = 3.20 \times 10^{-6} \text{ M}$, $[m\text{-HBA}] = 1.80 \times 10^{-2} \text{ M}$

the value of k_1 which was found to be in excellent agreement with all those values given in 2nd column of Table 4.7. This confirms that order of the reaction with respect to chloramine - T is one.

4.2 DETERMINATION OF THE ORDER OF THE REACTION WITH RESPECT TO m - HYDROXY BENZOIC ACID CONCENTRATION

This section deals with determination of order of the reaction respect to m - hydroxy benzoic acid. In order to ascertain the dependence of the reaction on substrate, reaction was studied at various concentrations of the reductant at fixed concentrations of all other reactants. In all experiments the concentration of chloramine - T has always been kept smaller than that of substrate in order to allow the isolation method applicable. The results obtained at 30° are given in the following tables.

TABLE 4.8

Temperature 30°

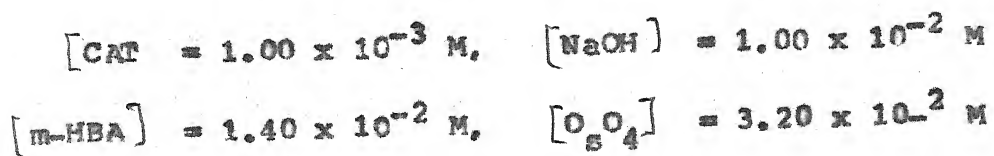
$$\begin{aligned}
 [\text{CAT}] &= 1.00 \times 10^{-3} \text{ M}, & [\text{NaOH}] &= 1.00 \times 10^{-2} \text{ M}, \\
 [\text{m-HBA}] &= 1.20 \times 10^{-2} \text{ M}, & [\text{O}_8\text{O}_4] &= 3.20 \times 10^6 \text{ M}
 \end{aligned}$$

Time (minutes)	ml of hypo solution ($2.00 \times 10^{-3} \text{ N}$)	$k_1 \times 10^4 \text{ min}^{-1}$
0	5.00	--
60	4.48	18.28
120	4.10	16.77
180	3.70	16.72
240	3.32	17.05
300	3.02	16.79
360	2.76	16.49
420	2.50	16.72
480	2.25	16.60

Average value of $k_1 = 16.93 \times 10^{-4} \text{ min}^{-1}$

TABLE 4.9

Temperature 30°



Time (minutes)	ml of hypo solution ($2.00 \times 10^{-3} \text{ N}$)	$k_1 \times 10^4 \text{ min}^{-1}$
0	5.00	--
60	4.40	21.28
120	3.90	20.58
180	3.46	20.44
240	3.04	20.44
300	2.66	21.01
360	2.32	21.32
420	2.06	21.09

Average value of $k_1 = 20.89 \times 10^{-4} \text{ min}^{-1}$

TABLE 4.10

Temperature 30°

$$[\text{CAT}] = 1.00 \times 10^{-3} \text{ M}, \quad [\text{NaOH}] = 1.00 \times 10^{-2} \text{ M}$$

$$[\text{m-HBA}] = 1.80 \times 10^{-2} \text{ M}, \quad [\text{O}_2\text{O}_4] = 3.20 \times 10^{-6} \text{ M}$$

Time (minutes)	ml of hypo solution ($2.00 \times 10^{-3} \text{ N}$)	$k_1 \times 10^4 \text{ min}^{-1}$
0	5.00	--
60	4.28	25.94
120	3.62	26.44
180	3.10	26.86
240	2.60	27.20
300	2.22	26.40
360	1.92	26.54
420	1.62	26.48
480	1.40	27.08

Average value of $k_1 = 26.62 \times 10^{-4} \text{ min}^{-1}$

TABLE 4.11

Temperature 30°

$$[\text{CAT}] = 1.00 \times 10^{-3} \text{ M}, \quad [\text{NaOH}] = 1.00 \times 10^{-2} \text{ M}$$

$$[\text{m-HBA}] = 2.20 \times 10^{-2} \text{ M}, \quad [\text{O}_2\text{O}_4] = 3.20 \times 10^{-6} \text{ M}$$

Time (minutes)	ml of hypo solution ($2.00 \times 10^{-3} \text{ N}$)	$k_1 \times 10^4 \text{ min}^{-1}$
0	5.00	- -
60	4.08	33.85
120	3.40	32.10
180	2.80	32.17
240	2.32	32.00
300	1.92	31.87
360	1.58	31.96
420	1.30	32.04
480	1.08	30.00

Average value of $k_1 = 32.00 \times 10^{-4} \text{ min}^{-1}$

TABLE 4.12
Temperature 30°

$$[\text{CAT}] = 1.00 \times 10^{-3} \text{ M}, \quad [\text{NaOH}] = 1.00 \times 10^{-2} \text{ M}$$

$$[\text{m-HBA}] = 3.40 \times 10^{-2} \text{ M}, \quad [\text{O}_2\text{O}_4] = 3.20 \times 10^{-6} \text{ M}$$

Time (minutes)	ml of hypo solution ($2.00 \times 10^{-3} \text{ N}$)	$k_1 \times 10^{-4} \text{ min}^{-1}$
0	5.00	--
30	4.26	52.82
60	3.64	52.86
90	3.10	52.80
120	2.70	51.29
150	2.44	51.18
180	1.96	52.00
240	1.40	52.98
300	1.06	51.68

Average value of $k_1 = 52.20 \times 10^{-4} \text{ min}^{-1}$

The results of tables 4.8 - 4.12 are summarised in
 Table 4.13.

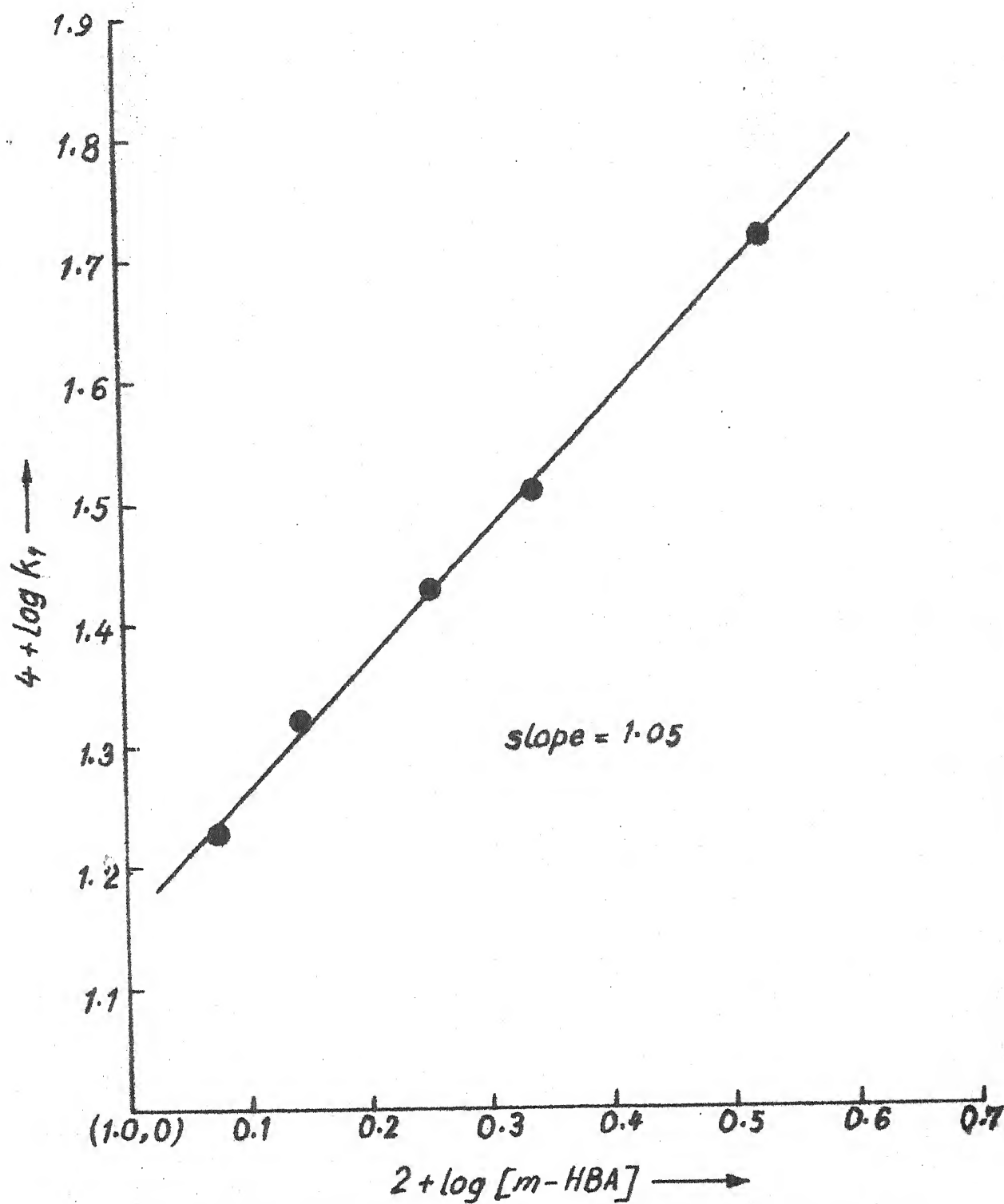


Fig. 4.2 : $[CAT] = 1.00 \times 10^{-3} M$, $[NaOH] = 1.00 \times 10^{-2} M$
 $[OsO_4] = 3.20 \times 10^{-6} M$, Temperature 30°

TABLE 4.13

$$[\text{CAT}] = 1.00 \times 10^{-3} \text{ M}, [\text{NaOH}] = 1.00 \times 10^{-2} \text{ M}$$

$$[\text{O}_3\text{O}_4] = 3.20 \times 10^{-6} \text{ M}, \text{ Temperature } 30^\circ$$

$[\text{m-HBA}] \times 10^2$ M	$k_1 \times 10^4$ min^{-1}	$k_2 \times 10^2 (k_2 = k_1 / [\text{m-HBA}])$ $\text{mole}^{-1} \text{ l min}^{-1}$
1.20	16.93	14.11
1.40	20.89	14.06
1.80	26.62	14.80
2.20	32.00	14.54
3.40	52.20	15.05

It is clear from the results of above table that on increasing the concentration of *m*-hydroxy benzoic acid, the value of first order rate constant i.e k_1 increases linearly. The almost constant values of k_2 (obtained on dividing k_1 values by $[\text{m-HBA}]$), the second order rate constant also indicate first-order dependence of the reaction on *m*-hydroxy benzoic acid.

The order of the reaction with respect to substrate is, further, confirmed by plotting a graph between $\log k_1$ and $\log [\text{m-HBA}]$. The slope of the curve (Fig.4.2) comes out to be 1.05 which shows that the reaction follows first - order kinetics with respect to *m* - hydroxy benzoic acid.

4.3 DETERMINATION OF THE ORDER OF THE REACTION WITH RESPECT TO ALKALI CONCENTRATION

In order to exactly ascertain the influence of the alkali concentration variation on the rate of oxidation of *m* - hydroxy benzoic acid by chloramine - T, a set of series of experiments has been performed at different concentrations ^{of} alkali keeping the concentrations of other reactants constant. The results obtained at 30° for varying concentrations of alkali are recorded in the following tables.

TABLE 4.14

Temperature 30°

$$[\text{CAT}] = 1.00 \times 10^{-3} \text{ M}, \quad [\text{NaOH}] = 0.65 \times 10^{-2} \text{ M}$$

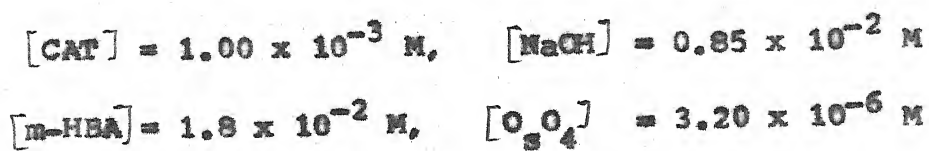
$$[\text{m-HBA}] = 1.8 \times 10^{-3} \text{ M}, \quad [\text{O}_2\text{O}_4] = 3.20 \times 10^{-6} \text{ M}$$

Time (minutes)	ml of hypo solution ($2.00 \times 10^{-3} \text{ M}$)	$k_1 \times 10^4 \text{ min}^{-1}$
0	5.00	--
30	4.32	48.30
60	3.74	48.34
90	3.30	46.13
120	2.82	47.67
150	2.48	46.86
180	2.14	47.09
240	1.64	46.40
300	1.24	46.43

Average value of $k_1 = 47.15 \times 10^{-4} \text{ min}^{-1}$

TABLE 4.15

Temperature 30°



Time (minutes)	ml of hypo solution ($2.00 \times 10^{-3} \text{ N}$)	$k_1 \times 10^4 \text{ min}^{-1}$
0	5.00	- -
30	4.46	38.34
60	4.00	37.14
90	3.54	38.33
120	3.20	37.14
180	2.64	35.44
240	2.14	35.32
300	1.76	34.76
360	1.38	35.72

Average value of $k_1 = 36.52 \times 10^{-4} \text{ min}^{-1}$

TABLE 4.16

Temperature 30°

$$[\text{CAT}] = 1.00 \times 10^{-3} \text{ M}, \quad [\text{NaOH}] = 1.00 \times 10^{-2} \text{ M}$$

$$[\text{m-HBA}] = 1.80 \times 10^{-2} \text{ M}, \quad [\text{O}_2\text{O}_4] = 3.20 \times 10^{-6} \text{ M}$$

Time (minutes)	ml of hypo solution ($2.00 \times 10^{-3} \text{ N}$)	$k_1 \times 10^4 \text{ min}^{-1}$
0	5.00	--
60	4.18	29.82
120	3.56	28.10
180	2.98	28.72
240	2.50	28.85
300	2.06	29.52
360	1.72	32.37
420	1.48	29.00
480	1.22	29.35

Average value of $k_1 = 29.46 \times 10^{-4} \text{ min}^{-1}$

TABLE 4.17

Temperature 30°

$$[\text{CAT}] = 1.00 \times 10^{-3} \text{ M}, \quad [\text{NaOH}] = 1.60 \times 10^{-2} \text{ M}$$

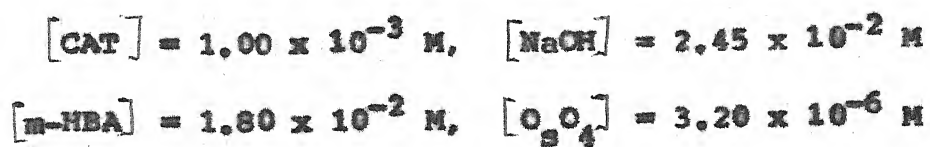
$$[\text{m-HBA}] = 1.80 \times 10^{-2} \text{ M}, \quad [\text{O}_2\text{O}_4] = 3.20 \times 10^{-6} \text{ M}$$

Time (minutes)	ml of hypo solution ($2.00 \times 10^{-3}\text{N}$)	$k_1 \times 10^4 \text{min}^{-1}$
0	5.00	- -
60	4.48	18.28
120	4.00	18.57
180	3.52	19.49
240	3.18	18.84
300	2.88	18.37
360	2.56	18.58
420	2.28	18.68
480	2.02	18.86

Average value of $k_1 = 18.71 \times 10^{-4} \text{min}^{-1}$

TABLE 4.18

Temperature 30°



Time (minutes)	ml of hypo solution ($2.00 \times 10^{-3} \text{ N}$)	$k_1 \times 10^4 \text{ min}^{-1}$
0	5.00	--
60	4.70	10.31
120	4.38	11.02
180	4.06	11.56
240	3.76	11.86
300	3.52	11.69
360	3.26	11.92
420	2.98	12.31
480	2.78	11.26

Average value of $k_1 = 11.49 \times 10^{-4} \text{ min}^{-1}$

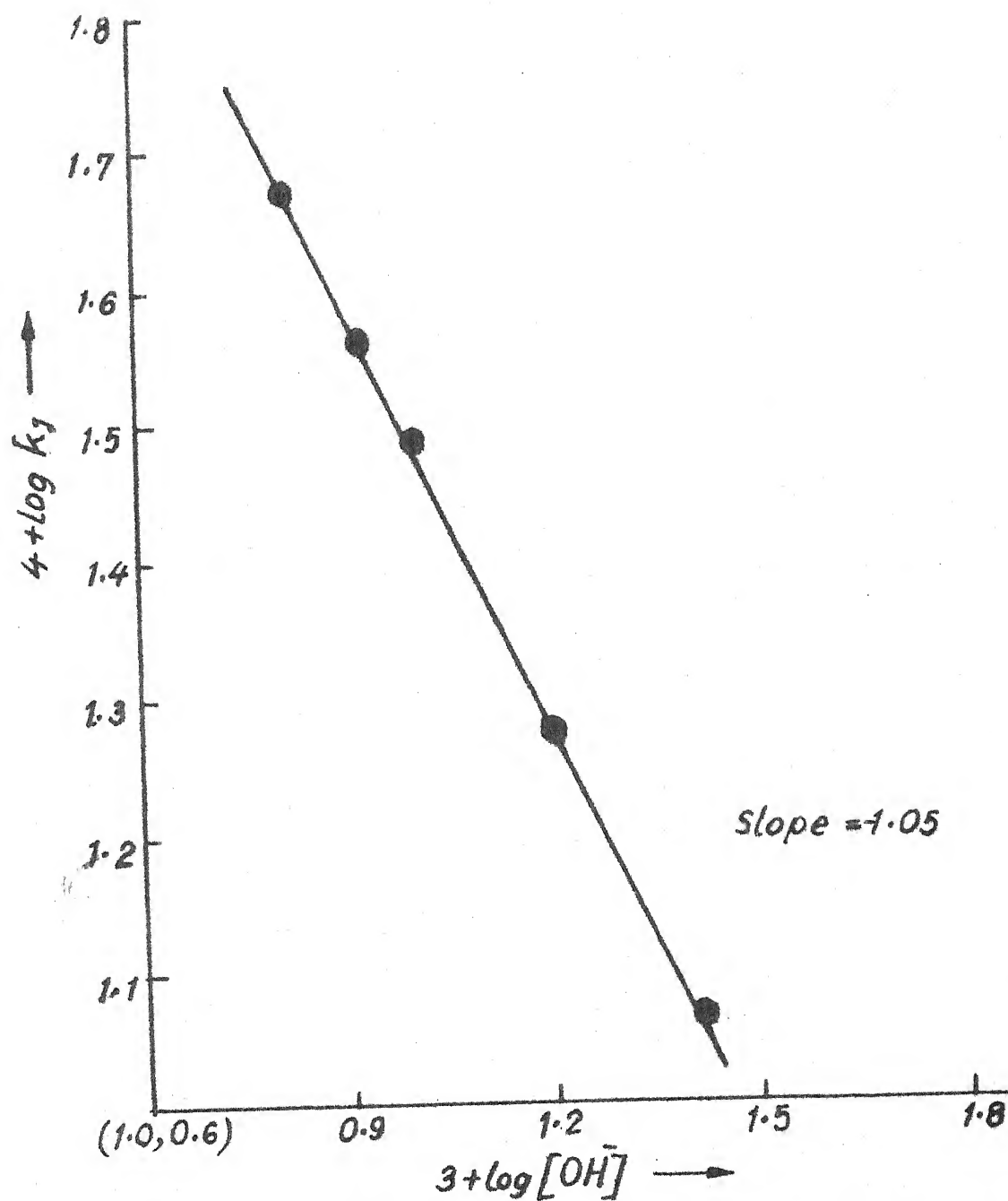


Fig. 4.3: $[\text{CAT}] = 1.00 \times 10^{-3} \text{ M}$, $[m\text{-HBA}] = 1.80 \times 10^{-2} \text{ M}$
 $[\text{OsO}_4] = 3.20 \times 10^{-6} \text{ M}$, Temperature 30°

The results recorded in tables 4.14 - 4.18 are given in a summarised form in Table 4.19.

TABLE 4.19

$$[\text{CAT}] = 1.00 \times 10^{-3} \text{ M}, [\text{m-HBA}] = 1.80 \times 10^{-2} \text{ M}$$

$$[\text{O}_3\text{O}_4] = 3.20 \times 10^{-6} \text{ M}, \text{ Temperature } 30^\circ$$

$[\text{NaOH}] \times 10^2$ M	$k_1 \times 10^4$ min^{-1}	$k_2 \times 10 (k_2 = k_1 / [\text{OH}^-])$ $\text{mole}^{-1} \text{ l min}^{-1}$
0.65	47.15	7.25
0.85	36.52	4.30
1.00	29.46	2.95
1.60	18.71	1.17
2.45	11.49	0.47

A careful perusal of results of table 4.19 indicates that on increasing alkali concentration k_1 values decreases. In order to ascertain the order with respect to alkali, $\log k_1$ values were plotted against $\log [\text{OH}^-]$ values (Fig.4.3). A straight line with slope equal to - 1.05 was obtained which proves that rate of the reaction is inversely proportional to alkali concentration.

4.4 DETERMINATION OF THE ORDER OF REACTION WITH RESPECT TO OSMIUM TETROXIDE CONCENTRATION

This section deals with the investigation on the effect of osmium tetroxide concentration on the rate of the reaction between m - hydroxy benzoic acid and alkaline - solution of chloramine - T. Various experiments at different concentrations of osmium tetroxide have been performed keeping the concentrations of other reactants constant and results are given in Table 4.20.

TABLE 4.20

$$\begin{aligned}
 [\text{CAT}] &= 1.00 \times 10^{-3} \text{ M}, & [\text{NaOH}] &= 1.00 \times 10^{-2} \text{ M} \\
 [\text{m-HBA}] &= 1.80 \times 10^{-2} \text{ M}, & \text{Temperature} &= 30^\circ
 \end{aligned}$$

$[\text{OsO}_4] \times 10^6 \text{ M}$	$k_1 \times 10^4 \text{ min}^{-1}$	$k_2 \times 10^{-2} \text{ l mole}^{-1} \text{ min}^{-1}$
0.75	06.02	8.02
1.50	12.48	8.32
2.00	16.52	8.26
2.50	20.40	8.16
3.20	26.60	8.31
4.00	32.80	8.20
4.50	36.45	8.10

A perusal of data of table 4.20 indicates that there is direct proportionality between the concentration of osmium tetroxide and first - order rate constant, showing, thereby first - order kinetics with respect to osmium tetroxide. The

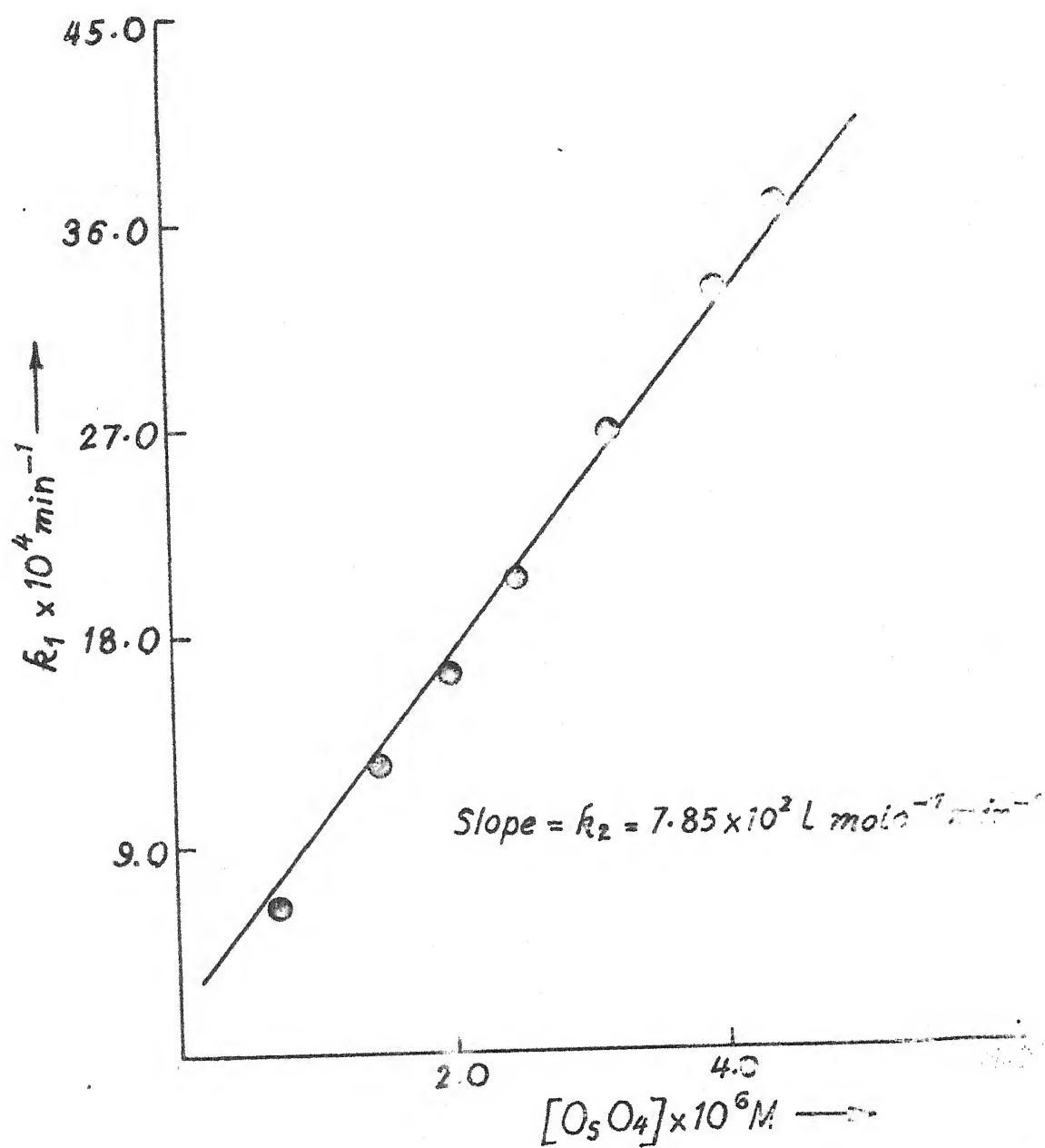


Fig. 4.4 : $[CAT] = 1.00 \times 10^{-3} \text{ M}$, $[NaOH] = 1.00 \times 10^{-2} \text{ M}$
 $[m\text{-HBA}] = 1.80 \times 10^{-2} \text{ M}$, Temperature 20°

second order rate constant i.e. k_2 values given in last column of above table are almost constant, which further indicates first - order dependence on osmium tetroxide concentration. A plot between k_1 values and $[O_3O_4]$ gives a straight line with a slope equal to (Fig.4.4) which is quite nearer to the values given in 3rd column of above table. This confirms that the order with respect to osmium tetroxide is one.

4.5 DETERMINATION OF THE EFFECT OF IONIC STRENGTH OF THE MEDIA ON REACTION VELOCITY

In most of the reactions, it has been observed that the reaction is influenced by increase in the concentration of salts added to the reaction mixture. Addition of salts also increases the ionic strength of the media whose effect on rate of the reaction gives some useful information required for identifying the nature of reactive species. The results obtained at various ionic strength of the medium (maintained by addition of suitable amounts of NaClO_4) are given in Table 4.21.

TABLE 4.21

Temperature 30°

$$[\text{CAT}] = 1.00 \times 10^{-3} \text{ M}, \quad [\text{NaOH}] = 1.00 \times 10^{-2} \text{ M}$$

$$[\text{m-HBA}] = 1.80 \times 10^{-2} \text{ M}, \quad [\text{O}_5\text{O}_4] = 3.20 \times 10^{-6} \text{ M}$$

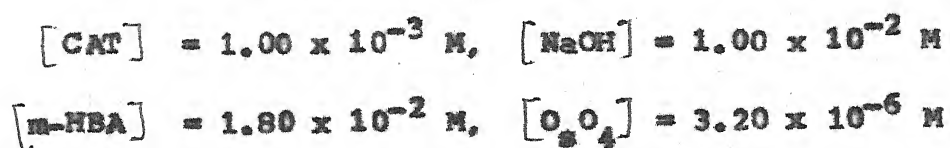
$[\text{NaClO}_4] \text{ M}$	Ionic Strength $\mu(\text{M})$	$k_1 \times 10^4 \text{ min}^{-1}$
0.0	0.11	26.60
0.20	0.21	26.58
0.30	0.31	26.61
0.40	0.41	26.62
0.50	0.51	26.56
0.60	0.61	26.63

It is evident from the results of above table that there is no significant effect of ionic strength variation on reaction velocity i.e. reaction velocity remains unaffected by ionic strength change.

4.6 DETERMINATION OF EFFECT OF SOLVENT VARIATION ON REACTION RATE

Kinetic data obtained at various methanol-water mixtures are summarised below.

TABLE 4.22



Temperature 30°

Methanol %(v/v)	$k_1 \times 10^4 \text{ min}^{-1}$
00	26.60
10	26.62
20	26.61
30	26.58
40	26.60

It is clear from the above table that the reaction rate is not influenced by variation in solvent composition.

4.7 DETERMINATION OF EFFECT OF VARIATION OF p - TOLUENE SULPHONAMIDE CONCENTRATION ON REACTION RATE

This section reports the kinetic data obtained at various initial concentrations of p-toluene sulphonamide (one of the reaction products) and results obtained are given in the following table.

TABLE 4.23

$$[\text{CAT}] = 1.00 \times 10^{-3} \text{ M}, \quad [\text{NaOH}] = 1.00 \times 10^{-2} \text{ M}$$

$$[\text{m-HBA}] = 1.80 \times 10^{-2} \text{ M}, \quad [\text{O}_2\text{O}_4] = 3.20 \times 10^{-6} \text{ M}$$

Temperature 30°C

$[\text{TSA}] \times 10^3 \text{ M}$	$k_1 \times 10^4 \text{ min}^{-1}$
0.0	26.58
0.25	26.62
0.50	26.60
0.75	26.59
1.00	26.61
1.50	26.62
2.00	26.59

It is obvious from the above table that k_1 values remain almost constant at all concentrations of p - toluene sulphonamide.

4.8 DETERMINATION OF EFFECT OF VARIATION OF TEMPERATURE ON REACTION RATE

In this section, an attempt has been made to investigate the effect of temperature variation on reaction rate. The reaction has been studied at 25, 30, 35 and 40°C. The result at 30° has already been reported. The results obtained at 25, 35 and 40° are reported in the following tables.

TABLE 4.24

Temperature 25°

$$[\text{CAT}] = 1.00 \times 10^{-3} \text{ M}, \quad [\text{NaOH}] = 1.00 \times 10^{-2} \text{ M},$$

$$[\text{m-HBA}] = 1.80 \times 10^{-2} \text{ and } [\text{O}_2\text{O}_4] = 3.20 \times 10^{-6} \text{ M}$$

Time (minutes)	ml of hypo solution ($2.00 \times 10^{-3}\text{N}$)	$k_1 \times 10^4 \text{min}^{-1}$
0	5.00	--
60	4.48	13.31
120	3.92	20.28
180	3.42	21.11
240	3.02	21.01
300	2.60	21.80
360	2.32	21.33
420	2.06	21.16
500	1.68	22.07

Average value of $k_1 = 20.88 \times 10^{-4}$

TABLE 4.25

Temperature 35°

 $[\text{CAT}] = 1.00 \times 10^{-3} \text{ M}, \quad [\text{NaOH}] = 1.00 \times 10^{-2} \text{ M}$ $[\text{m-HBA}] = 1.80 \times 10^{-2} \text{ M}$ and $[\text{O}_8\text{O}_4] = 3.20 \times 10^{-6} \text{ M}$

Time (minutes)	Volume of hypo solution($2.00 \times 10^{-3} \text{ N}$)	$k_1 \times 10^4 \text{ min}^{-1}$
0	5.00	- -
60	4.14	31.47
120	3.42	31.67
180	2.80	32.22
240	2.32	32.00
300	1.92	31.91
360	1.60	31.60
420	1.28	32.45
500	1.00	32.20

Average value of $k_1 = 31.95 \times 10^4 \text{ min}^{-1}$

TABLE 4.26

Temperature 40°

$$[\text{CAT}] = 1.00 \times 10^{-3} \text{ M}, \quad [\text{NaOH}] = 1.00 \times 10^{-2} \text{ M}$$

$$[\text{m-HBA}] = 1.80 \times 10^{-2} \text{ M} \quad \& \quad [\text{O}_3\text{O}_4] = 3.20 \times 10^{-6} \text{ M}$$

Time (minutes)	Volume of hypo solution ($2.00 \times 10^{-3} \text{ N}$)	$k_1 \times 10^4 \text{ min}^{-1}$
0	5.00	--
60	4.04	35.54
120	3.24	35.18
180	2.60	36.34
240	2.14	35.37
300	1.73	35.58
360	1.42	34.97
420	1.14	35.20

Average value of $k_1 = 35.45 \times 10^{-4} \text{ min}^{-1}$

The values of first - order constants obtained in above tables and Table 4.2 are summarised in the following table.

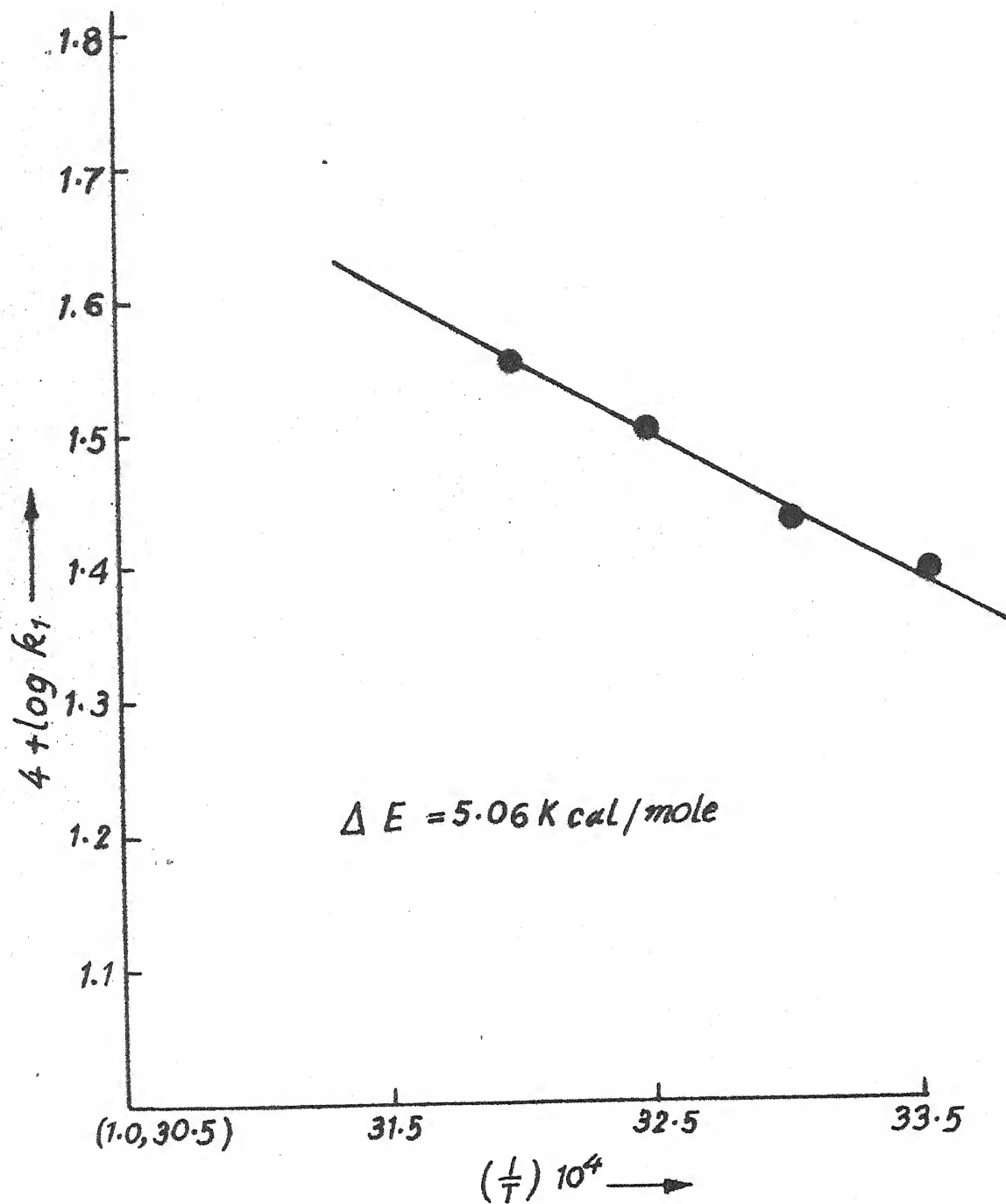
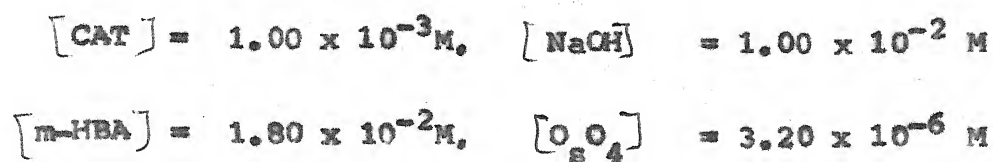


Fig. 4.5 $[\text{CAT}] = 1.00 \times 10^{-3} \text{ M}$, $[\text{NaOH}] = 1.00 \times 10^{-2} \text{ M}$
 $[\text{m-HBA}] = 1.80 \times 10^{-2} \text{ M}$, $[\text{O}_5\text{O}_4] = 3.20 \times 10^{-6} \text{ M}$

TABLE 4.27

Temperature °C	$k_1 \times 10^4 \text{ min}^{-1}$
25	20.88
30	26.63
35	31.95
40	35.45

Results of above table have been utilised to calculate the value of energy of activation i.e. ΔE . The slope of the curve obtained from the graph between $\log k_1$ and $\frac{1}{T}$ values (Fig.4.5) gave $-\frac{\Delta E}{2.303R}$ according to Arrhenius equation

$$\log k = \log A - \frac{\Delta E}{2.303 RT}$$

The value of ΔE was thus calculated from slope and was found to be 5.06 K cal/mole.

C H A P T E R V

KINETICS OF OSMIUM TETROXIDE CATALYSED
OXIDATION OF 4 - BUTYL MORPHOLINE BY
ALKALINE HEXACYANOFERRATE (III)

This chapter deals with the study of oxidation of 4-butyl morpholine by aqueous alkaline solution of potassium hexacyanoferrate (III) in the presence of osmium tetroxide as catalyst. Isolation method was employed to study the kinetics of the reaction between 4-butyl morpholine and hexacyanoferrate(III) ions. In all sets of experiments performed in this chapter, the concentrations of hexacyanoferrate(III) was always kept smaller as compared to that of 4-butyl morpholine to allow the application of isolation method. Here also, no buffer could be used due to high alkali concentration. This chapter has been divided in many sections. Each section deals with the dependence of the reaction on varying the concentration of each reactant and other variable parameters e.g. temperature variation, ionic strength variation etc.

5.1 STUDY OF EFFECT OF VARIATION OF [HEXACYANOFERRATE(III)] ION ON REACTION VELOCITY

In this section, an attempt has been made to investigate the order of the reaction with respect to hexacyanoferrate(III) ion. In order to do so, the reaction has been studied at various concentrations of hexacyanoferrate(III) ion by keeping the concentration of other reactants ^{constant} and results obtained are presented in the following tables.

TABLE 5.1

Temperature 30°

$$[K_3 Fe (CN)_6] = 1.00 \times 10^{-3} \text{ M}, [NaOH] = 7.50 \times 10^{-2} \text{ M}$$

$$[4 - \text{Butyl morpholine}] = 1.00 \times 10^{-2} \text{ M}, [O_8O_4] = 15.60 \times 10^{-6} \text{ M}$$

Time (minutes)	Volume of Ceric sulphate ($9.4 \times 10^{-4} \text{ M}$) in ml	$\frac{\Delta x}{\Delta t} \times 10^2$ ml/min
0	0.00	--
5	0.50	10.00*
10	0.82	6.40
15	1.14	6.40
20	1.46	6.40
25	1.82	7.20
30	2.16	6.80
40	2.76	6.00
50	3.42	6.60
60	4.10	6.80
100	5.32	--

Average k_0 value (neglecting*) = $6.58 \times 10^{-2} \text{ ml/min.}$

$$k_s = \frac{k_0 \times s}{V} = 12.37 \times 10^{-6} \text{ mole lit}^{-1} \text{ min}^{-1}$$

Second column of the above table containing the concentration of hexacyanoferrate(III) in terms of ceric sulphate concentration shows the progress of the reaction. Third column of above table shows the ml of ceric sulphate used for hexacyanoferrate(II) produced per minute. A perusal of data in 3rd column indicates a zero ~~order~~ dependence of the reaction on hexacyanoferrate(III) concentration. At the bottom of the table average value of zero-order rate constant k_b ($\frac{\Delta x}{\Delta t}$) has been given. The value of standard zero - order rate constant (k_s) calculated from the value of k_o (as given below is also recorded.

$$k_s = k_o \times S/V$$

where S represents the concentration of ceric (IV) sulphate used and V, the volume of reaction mixture sucked to measure the reaction velocity. The k_s value represents the moles of hexacyanoferrate (II) formed per minute.

The following tables contain the data at different concentrations of hexacyanoferrate (III).

TABLE 5.2

Temperature 30°

 $[K_3 Fe (CN)_6] = 0.92 \times 10^{-3} M, [NaOH] = 7.50 \times 10^{-2} M$
 $[4\text{-Butyl morpholine}] = 1.00 \times 10^{-2} M, [O_2O_4] = 15.60 \times 10^{-6} M$

Time (minute)	Volume of cerit sulphate ($8.20 \times 10^{-4} M$) in ml	$\frac{\Delta X}{\Delta t} \times 10^{12}$ ml/min
0	0.00	--
5	0.60	12.00
10	1.00	8.00
15	1.38	7.60
20	1.74	7.20
25	2.10	7.20
30	2.48	7.60
35	2.86	7.60
40	3.24	7.60
50	4.04	8.00
T	5.02	--

Average value of k_o (neglecting *) = 7.60×10^{-2} ml/min

$k_s = k_o \times S/V = 12.48 \times 10^{-6}$ mole lit⁻¹ min⁻¹

TABLE 5.3

Temperature 30°

$$[K_3Fe(CN)_6] = 1.34 \times 10^{-3} \text{ M}, [NaOH] = 7.50 \times 10^{-2} \text{ M}$$

$$[4\text{-Butyl morpholine}] = 1.00 \times 10^{-2} \text{ M}, [O_2O_4] = 15.60 \times 10^{-6} \text{ M}$$

Time (minutes)	Volume of Ceric sulphate (9.4×10^{-4} M) in ml	$\frac{\Delta X}{\Delta t} \times 10^2$ ml/min
0	0.00	--
5	0.50	10.00*
10	0.82	6.40
15	1.16	6.80
20	1.48	6.40
30	2.18	7.00
40	2.84	6.60
50	3.50	6.60
60	4.14	6.40
70	4.78	6.40
T	7.12	--

Average k_o value (neglecting*) = 6.58×10^{-2} ml/min

$$k_s = k_o \times S/V = 12.37 \times 10^{-6} \text{ mole lit}^{-1} \text{ min}^{-1}$$

TABLE 5.4

Temperature 30°

$$[K_3Fe(CN)_6] = 1.66 \times 10^{-2} \text{ M}, [NaOH] = 7.50 \times 10^{-2} \text{ M}$$

$$[4\text{-Butyl morpholine}] = 1.00 \times 10^{-2} \text{ M}, [O_8O_4] = 15.60 \times 10^{-6} \text{ M}$$

Time (minute)	Volume of Cerit sulphate ($9.40 \times 10^{-4} \text{ M}$) in ml	$\frac{\Delta X}{\Delta t} \times 10^2$ ml /min
0	0.00	--
5	0.56	11.20*
10	0.88	6.40
20	1.54	6.60
30	2.18	6.40
40	2.80	6.20
50	3.50	7.00
60	4.16	6.60
70	4.82	6.60
80	5.48	6.60
T	8.94	--

Average k_o value (neglecting*) = $6.55 \times 10^{-2} \text{ ml/min}$

$$k_s = k_o \times S/V = 12.31 \times 10^{-6} \text{ mole lit}^{-1} \text{ min}^{-1}$$

TABLE 5.5

Temperature 30°

$$[K_3Fe(CN)_6] = 2.00 \times 10^{-3} M, [NaOH] = 7.50 \times 10^{-2} M$$

$$[4\text{-Butyl morpholine}] = 1.00 \times 10^{-2} M, [O_3O_4] = 15.60 \times 10^{-6} M$$

Time (minute)	Volume of Ceric sulphate (9.40×10^{-4}) in ml	$\frac{\Delta X}{\Delta t} \times 10^2$ ml/min
0	0.00	--
5	0.56	11.20*
10	0.90	6.80
15	1.24	6.0
20	1.56	6.40
25	1.88	6.40
35	2.52	6.40
45	3.28	6.60
60	4.18	6.66
80	5.44	6.30
100	6.72	6.40
T	10.64	--

Average k_o value (neglecting*) = 6.52×10^{-2} ml/min

$$k_s = k_o \times S/V = 12.26 \times 10^{-6} \text{ mole lit}^{-1} \text{ min}^{-1}$$

TABLE 5.6

Temperature 30°

$$[K_3Fe(CN)_6] = 2.50 \times 10^{-3} M, [NaOH] = 7.50 \times 10^{-2} M$$

$$[4\text{-Butyl morpholine}] = 1.00 \times 10^{-1} M, [O_2O_4] = 15.60 \times 10^{-6} M$$

Time (minute)	Volume of Ceric sulphate ($9.40 \times 10^{-4} M$) in ml	$\frac{\Delta X}{\Delta t} \times 10^2$ ml / min
0	0.00	--
5	0.58	11.60
10	0.92	6.80
15	1.24	6.40
20	1.58	6.80
30	2.24	6.60
40	2.92	6.80
50	3.58	6.60
80	5.62	6.80
110	7.56	6.46
T	13.30	--

Average k_0 value (neglecting *) = 6.66×10^{-2} ml/min

$$k_s = k_0 \times S/V = 12.40 \times 10^{-6} \text{ mole lit}^{-1} \text{ min}^{-1}$$

TABLE 5.7

Temperature 30°

$$[K_3Fe(CN)_6] = 3.34 \times 10^{-3} M, [NaOH] = 7.50 \times 10^{-2} M$$

$$[4 \text{ Butyl morpholine}] = 1.00 \times 10^{-2} M, [O_2O_4] = 15.60 \times 10^{-6} M$$

Time (minutes)	Volume of Ceric sulphate ($2.00 \times 10^{-3} M$) in ml)	$\frac{\Delta x}{\Delta t} = 10^{-2}$ ml / min
0	0.00	--
5	0.30	6.00 *
10	0.46	3.20
15	0.62	3.20
25	0.90	2.80
35	1.22	3.20
50	1.68	3.06
70	2.28	3.00
100	3.12	2.80
135	4.12	2.86
175	5.32	3.00
T	8.36	--

Average k_0 value (neglecting*) = 3.02×10^{-2} ml/min

$$k_s = k_0 \times S/V = 12.08 \times 10^{-6} \text{ mole lit}^{-1} \text{ min}^{-1}$$

The results of Tables 5.1 - 5.7 were summarised in Table 5.8.

TABLE 5.8

Temperature 30°

$$[4\text{-Butyl morpholine}] = 1.00 \times 10^{-2} \text{ M}$$

$$[\text{NaOH}] = 7.50 \times 10^{-2} \text{ M}$$

$$[\text{O}_2\text{O}_4] = 15.60 \times 10^{-6} \text{ M}$$

$[\text{K}_3\text{Fe}(\text{CN})_6] \times 10^3 \text{ M}$	$k_s (\text{from } k_o) \times 10^6$ mole lit ⁻¹ min ⁻¹	$k_s (\text{graptical}) \times 10^6$ mole lit ⁻¹ min ⁻¹
0.82	12.48	12.50
1.00	12.37	12.48
1.34	12.37	12.87
1.66	12.31	12.45
2.00	12.26	12.50
2.50	12.40	13.75
3.34	12.08	13.15

It is clear from the results of above table that k_s values are almost constant at all initial concentrations of hexacyanoferrate (III), which shows that reaction follows zero - order kinetics in hexacyanoferrate(III).

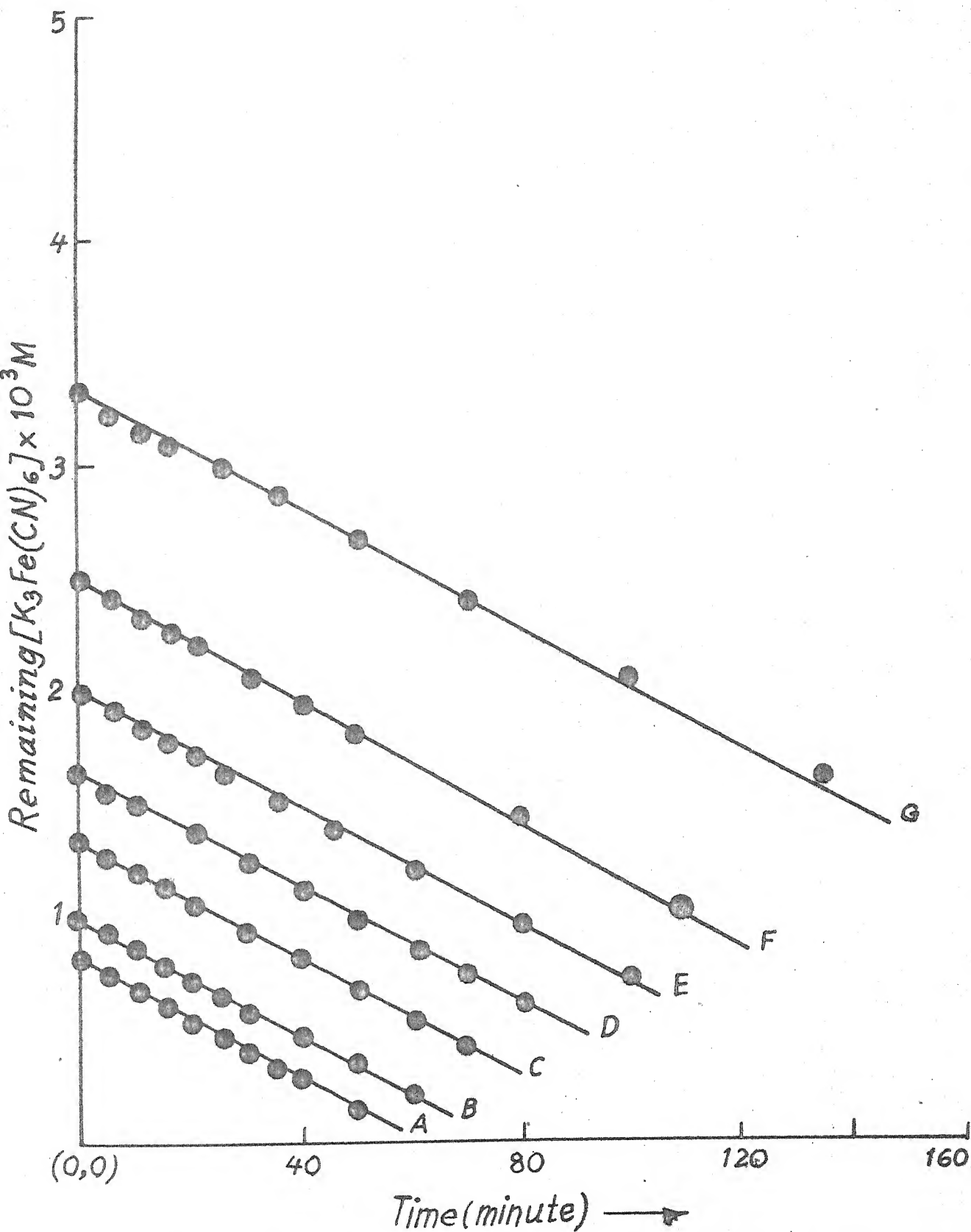


Fig.5.1: $[4\text{-Butylmorpholine}] = 1.00 \times 10^{-2} M$; $[NaOH] = 7.50 \times 10^{-2} M$,
 $[O_5O_4] = 15.60 \times 10^{-6} M$, Temperature 30°
 $[K_3Fe(CN)_6] = 0.82(A), 1.00(B), 1.34(C), 1.66(D)$
 $2.00(E), 2.50(F)$ and $3.34 \times 10^{-3} M (G)$

In order to, further, confirm the order in oxidants, graphs between remaining $[\text{Hexacyanoferrate (III)}]$ and time were plotted. Straight lines (Fig.5.1) were obtained, the slope of which gave k_s values. A perusal of k_s values from graph recorded in 3rd column of table 5.8 clearly indicates that these values are quite close to k_s values given in 2nd column of table 5.8 and are also ²pattically ₁constant confirming, thereby, zero-order dependence on the reaction.

5.2 STUDY OF EFFECT OF VARIATION OF [4 - BUTYL MORPHOLINE] ON VELOCITY

This section deals with the dependence of oxidation of the substrate by hexacyanoferrate (III) ion in alkaline media in the presence of osmium tetroxide on 4 - butyl morpholine. In order to achieve this aim, the reaction has been studied at different concentrations of 4 - butyl morpholine by keeping the concentrations of other reactants constant. The results obtained are recorded in the following tables.

TABLE 5.9

Temperature 35°

$$[4\text{-Butyl morpholine}] = 0.80 \times 10^{-2} \text{M}, [\text{NaOH}] = 7.50 \times 10^{-2} \text{M}$$

$$[\text{K}_3\text{Fe}(\text{CN})_6] = 2.00 \times 10^{-3} \text{M}, [\text{OsO}_4] = 9.45 \times 10^{-6} \text{M}$$

Time (minutes)	volume of ceric sulphate ($9.40 \times 10^{-4} \text{M}$) in ml	$\frac{\Delta X}{\Delta t} \times 10^2$ ml / min
0	0.00	- -
5	0.44	8.80*
10	0.60	3.20
15	0.75	3.00
20	0.92	3.40
30	1.24	3.20
40	1.54	3.00
50	1.88	3.40
70	2.56	3.40
100	3.52	3.20
140	4.72	3.00
T	10.64	- -

Average k_o value (neglecting *) = 3.20×10^{-2}

$$k_s = k_o \times S/V = 6.20 \times 10^{-6} \text{ mole lit}^{-1} \text{ min}^{-1}$$

TABLE 5.10

Temperature 35°

[4 - Butyl morpholine] = $1.00 \times 10^{-2} \text{M}$ [NaOH] = $7.50 \times 10^{-2} \text{M}$ [$\text{K}_3\text{Fe}(\text{CN})_6$] = $2.00 \times 10^{-3} \text{M}$, [O_2O_4] = $9.45 \times 10^{-6} \text{M}$

Time (minutes)	Volume of Ceric sulphate ($9.40 \times 10^{-4} \text{M}$) in ml	$\frac{\Delta B}{\Delta t} \times 10^2$ ml / min
0	0.00	- -
5	0.48	9.60 *
10	0.68	4.00
15	0.88	4.00
25	1.26	3.80
40	1.84	3.86
70	2.98	3.80
100	4.14	3.86
140	5.58	3.60
200	7.98	4.00
T	10.64	- -

Average k_0 value (except *) = $3.86 \times 10^{-2} \text{ ml/min}$ $k_s = 7.24 \times 10^{-6} \text{ mole lit}^{-1} \text{ min}^{-1}$

TABLE 5.11

Temperature 35°

[4 - Butyl morpholine] = $1.25 \times 10^{-2} \text{M}$, [NaOH] = $7.50 \times 10^{-2} \text{M}$ [$\text{K}_3\text{Fe}(\text{CN})_6$] = $2.00 \times 10^{-3} \text{M}$, [O_2O_4] = $9.45 \times 10^{-6} \text{M}$

Time (minute)	Volume of ceric sulphate ($9.40 \times 10^{-4} \text{M}$) in ml	$\frac{\Delta X}{\Delta t} \times 10^2$ ml / min
0	0.00	--
5	0.50	10.00*
10	0.76	15.20
15	1.00	4.80
20	1.24	4.80
30	1.70	4.60
40	2.16	4.60
60	3.10	4.70
90	4.54	4.80
125	6.22	4.80
150	7.86	4.68
T	10.64	--

Average value of k_0 (except *) = $4.78 \times 10^{-2} \text{ ml/min}$ $k_s = 8.98 \times 10^{-6} \text{ mole lit}^{-1} \text{ min}^{-1}$

TABLE 5.12

Temperature 35°

[4 - Butyl morpholine] = 1.66×10^{-2} M, [NaOH] = 7.50×10^{-2} M[K₃Fe(CN)₆] = 2.00×10^{-3} M, [O₂O₄] = 9.45×10^{-6} M

Time (minute)	Volume of ceric sulphate (9.40×10^{-4} M) in ml	$\frac{\Delta X}{\Delta t} \times 10^2$ ml / min
0	0.00	--
5	0.60	12.00*
10	0.94	6.80
15	1.26	6.40
20	1.58	6.40
30	2.20	6.20
45	3.16	6.40
60	4.10	6.26
90	6.02	6.40
120	7.90	6.26
150	9.90	6.34
T	10.64	--

Average value of k_o (except*) = 6.38×10^{-2} ml/min $k_s = 12.03 \times 10^{-6}$ mole lit⁻¹ min⁻¹

TABLE 5.13

Temperature 35°

[4-Butyl morpholine] = 2.00×10^{-2} M, [NaOH] = 7.50×10^{-2} M[$K_3Fe(CN)_6$] = 2.00×10^{-3} M, [O_2O_4] = 9.45×10^{-6} M

Time (minutes)	Volume of ceric sulphate (9.40×10^{-4} M) in ml	$\frac{\Delta X}{\Delta t} \times 10^2$ ml/min
0	0.00	- -
5	0.72	14.40
10	1.10	7.60
15	1.46	7.20
20	1.84	7.60
30	2.58	7.40
40	3.30	7.20
50	4.04	7.40
65	5.16	7.46
80	6.28	7.46
100	7.74	7.30
T	10.64	- -

Average value of k_o (except *) = 7.40×10^{-2} ml/min $k_s = 13.91 \times 10^{-6}$ mole lit⁻¹ min⁻¹

TABLE 5.14

Temperature 35°

[4 - Butyl morpholine] = 2.50×10^{-2} M, [NaOH] = 7.50×10^{-2} M[K₃Fe(CN)₆] = 2.00×10^{-3} M, [O₂] = 9.45×10^{-6} M

Time (minutes)	Volume of ceric sulphate (9.40×10^{-4} M) in ml	$\frac{x}{t} \times 10^2$ ml min ⁻¹
0	0.00	- -
5	0.86	17.20*
10	1.34	9.60
15	1.80	9.20
20	2.26	9.20
30	3.20	9.40
40	4.16	9.60
50	5.10	9.40
60	6.06	9.60
70	7.00	9.40
80	7.92	9.20
T	10.64	- -

Average value of k_o (except *) = 9.40×10^{-2} ml/min $k_s = 17.67 \times 10^{-6}$ mole lit⁻¹ min⁻¹

TABLE 5.15

Temperature 35°

 $[4\text{-Butyl morpholine}] = 5.00 \times 10^{-2} \text{M}$, $[\text{NaOH}] = 7.50 \times 10^{-2} \text{M}$ $[\text{K}_3\text{Fe}(\text{CN})_6] = 2.00 \times 10^{-3} \text{M}$, $[\text{O}_2\text{O}_4] = 9.45 \times 10^{-6} \text{M}$

Time (minute)	Volume of Ceric sulphate ($9.40 \times 10^{-4} \text{M}$) in ml	$\frac{\Delta X}{\Delta t} \times 10^2$ ml / min
0	0.00	--
5.	1.48	29.60*
10	2.44	19.20
15	3.40	19.20
20	4.38	19.60
25	5.32	18.80
30	6.28	19.20
35	7.24	19.20
40	8.18	18.80
45	9.14	19.20
T	10.64	--

Average k_0 value (except *) = $19.38 \times 10^{-2} \text{ ml/min}$ $k_s = 36.43 \times 10^{-6} \text{ mole lit}^{-1} \text{ min}^{-1}$

The results of tables 5.9 to 5.15 are summarised in the following table.

TABLE 5.16

$$[\text{K}_3\text{Fe}(\text{CN})_6] = 2.00 \times 10^{-3} \text{ M}, [\text{O}_2\text{O}_4] = 9.45 \times 10^{-6} \text{ M}$$

$$[\text{NaOH}] = 7.50 \times 10^{-2} \text{ M}, \text{ Temperature } 35^\circ$$

$[\text{4-Butyl morpholine}] \times 10^2$	$k_s (\text{from } k_o) \times 10^6$ mole lit ⁻¹ min ⁻¹	$10^4 k_1 = \frac{k_s}{[\text{Substrate}]}$ min ⁻¹
0.80	6.20	7.75
1.00	7.24	7.24
1.25	8.98	7.20
1.66	12.03	7.24
2.00	13.91	6.96
2.50	17.67	7.07
5.00	36.42	7.29

Average value of $k_1 = 7.25 \times 10^{-4} \text{ min}^{-1}$

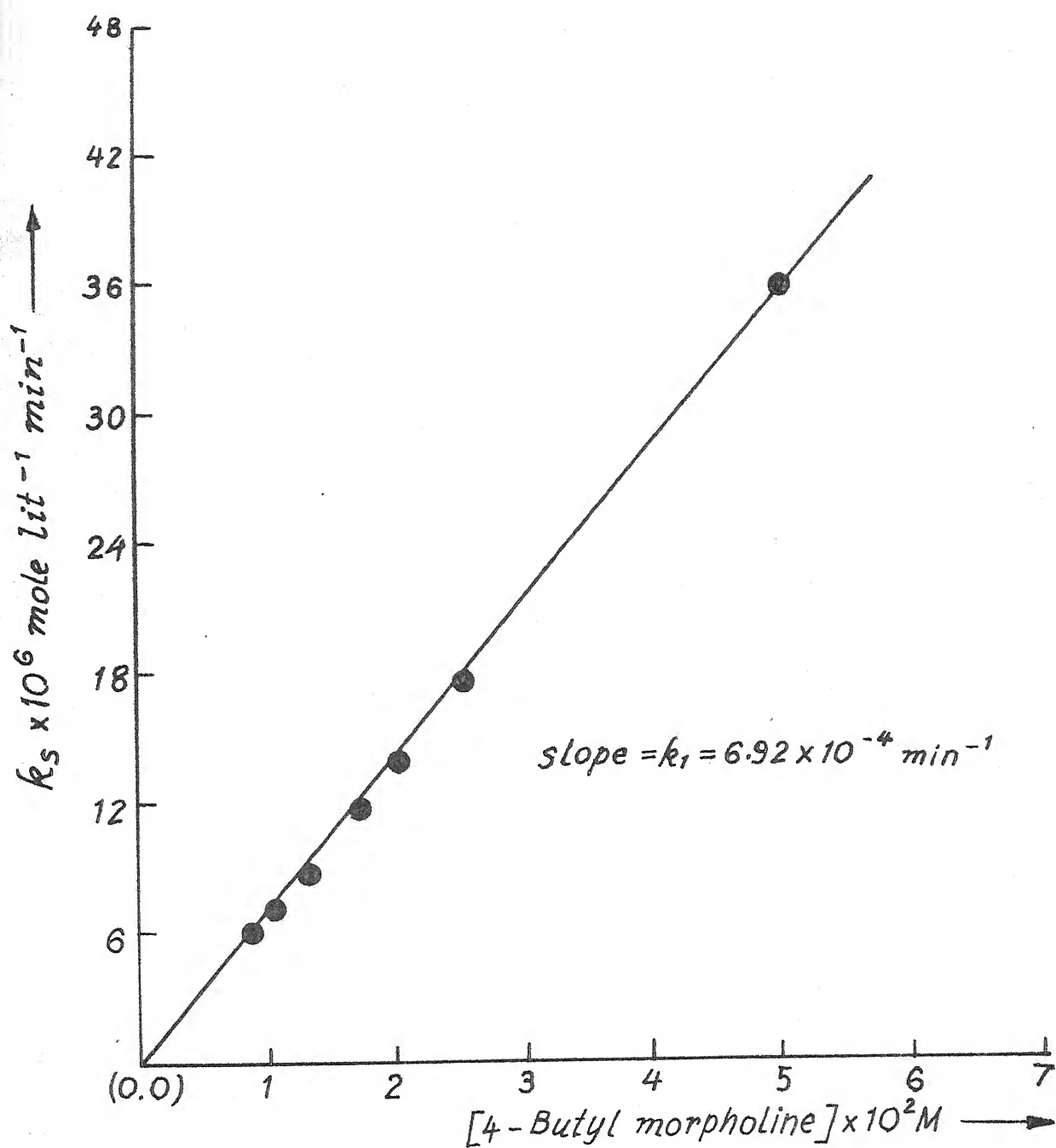


Fig.5.2: $[K_3Fe(CN)_6] = 2.00 \times 10^{-3} \text{ M}$, $[O_5O_4] = 9.45 \times 10^{-6} \text{ M}$
 $[NaOH] = 7.50 \times 10^{-2} \text{ M}$, Temperature 35°

A careful perusal of results of table 5.16 indicates that k_s values for molar concentration of 4 - butyl morpholine are almost constant, indicating first order dependence of the reaction on 4-butyl morpholine. This observation is, further confirmed graphically. A graph between [4 - butyl morpholine] and k_s values gives a straight line (Fig.5.2) passing through origin, suggesting first - order kinetics in 4 - butyl morpholine. The slope of the curve gives k_1 value equal to $6.92 \times 10^{-4} \text{ min}^{-1}$ which is nearer to k_1 value given in table 5.16.

5.3 STUDY OF EFFECT OF VARIATION OF [SODIUM HYDROXIDE] ON REACTION VELOCITY

In order to determine the dependence of the reaction on alkali concentration, a series of experiments have been carried out at different initial concentrations of sodium hydroxide but at fixed concentration of all other reactants. The results are given in tables 5.17 - 5.21.

TABLE 5.17

Temperature 35°

$$[K_3Fe(CN)_6] = 2.00 \times 10^{-3} M, [NaOH] = 2.5 \times 10^{-2} M$$

$$[4 - \text{Butyl morpholine}] = 2.00 \times 10^{-2} M, [O_2O_4] = 9.45 \times 10^{-6} M$$

Time (minutes)	Volume of ceric sulphate ($9.4 \times 10^{-4} M$) in ml	$\frac{\Delta X}{\Delta t} \times 10^2$ ml / min
0	0.00	--
5	0.40	8.00*
10	0.52	2.40
20	0.74	2.20
30	0.98	2.40
45	1.34	2.40
60	1.68	2.26
90	2.40	2.40
120	3.16	2.53
150	3.90	2.46
180	4.62	2.40
T	10.64	--

Average k_0 value (except *) = 2.38×10^{-2} ml/min

$$k_s = 4.47 \times 10^{-6} \text{ mole lit}^{-1} \text{ min}^{-1}$$

TABLE 5.18

Temperature 35°

$$[K_3Fe(CN)_6] = 2.00 \times 10^{-3} \text{ M}, [NaOH] = 5.00 \times 10^{-2} \text{ M}$$

$$[4 - \text{Butyl morpholine}] = 2.00 \times 10^{-2} \text{ M}, [C_8O_4] = 9.45 \times 10^{-6} \text{ M}$$

Time (minutes)	Volume of ceric sulphate ($9.40 \times 10^{-4} \text{ M}$) in ml	$\frac{\Delta X}{\Delta t} \times 10^2$ ml / min
0	0.00	- -
5	0.62	12.40*
10	0.86	4.80
20	1.36	5.00
30	1.86	5.00
45	2.60	4.93
60	3.32	4.80
80	4.30	4.90
100	5.30	5.00
140	7.24	4.85
180	9.16	4.80
T	10.64	- -

Average value of k_o (except *) = $4.90 \times 10^{-2} \text{ ml/min}$

$$k_s = 9.21 \times 10^{-6} \text{ mole lit}^{-1} \text{ min}^{-1}$$

TABLE 5.19

Temperature 35°

 $[K_3Fe(CN)_6] = 2.00 \times 10^{-3} \text{ M}, [NaOH] = 10.00 \times 10^{-2} \text{ M}$
 $[4 - \text{Butyl morpholine}] = 2.00 \times 10^{-2} \text{ M}, [O_8O_4] = 9.45 \times 10^{-6} \text{ M}$

Time (minute)	Volume of ceric sulphate ($9.40 \times 10^{-4} \text{ M}$) in ml	$\frac{\Delta x}{\Delta t} \times 10^2$ ml / min
0	0.00	--
5	0.60	16.00*
10	1.30	10.00
15	1.82	10.40
20	2.30	9.60
25	2.78	9.60
30	3.28	10.00
40	4.26	9.80
50	5.24	9.80
60	6.20	9.60
T	10.64	--

Average value of k_o (except *) = $9.85 \times 10^{-2} \text{ ml/min}$

$k_s = 18.52 \times 10^{-6} \text{ mole lit}^{-1} \text{ min}^{-1}$

TABLE 5.20

Temperature 35°

$$[K_3Fe(CN)_6] = 2.00 \times 10^{-3} M, [NaOH] = 12.50 \times 10^{-2} M$$

$$[4\text{-Butyl morpholine}] = 2.00 \times 10^{-2} M, [O_3O_4] = 9.45 \times 10^{-6} M$$

Time (minutes)	Volume of ceric sulphate ($9.40 \times 10^{-4} M$) in ml	$\frac{\Delta x}{\Delta t} \times 10^2$ ml / min
0	0.00	--
5	1.20	24.00*
10	1.84	12.80
15	2.46	12.40
20	3.06	12.00
25	3.68	12.40
30	4.30	12.40
40	5.50	12.00
50	6.76	12.60
60	8.00	12.40
T	10.64	--

Average value of k_o (except *) = 12.38×10^{-2} ml/min

$$k_s = 23.27 \times 10^{-6} \text{ mole lit}^{-1} \text{ min}^{-1}$$

TABLE 5.21

Temperature 35°

$$[\text{K}_3\text{Fe}(\text{CN})_6] = 2.00 \times 10^{-3} \text{ M}, [\text{NaOH}] = 15.00 \times 10^{-2} \text{ M}$$

$$[\text{4-Butyl morpholine}] = 2.00 \times 10^{-2} \text{ M}, [\text{O}_2\text{O}_4] = 9.45 \times 10^{-6} \text{ M}$$

Time (minute)	Volume of ceric sulphate ($9.40 \times 10^{-4} \text{ M}$) in ml	$\frac{\Delta X}{\Delta t} \times 10^2$ ml / min
0	0.00	- -
5	1.24	24.80 *
10	2.00	15.20
15	2.74	14.80
20	3.50	15.20
25	4.24	14.80
35	5.74	15.00
45	7.24	15.00
60	9.46	14.80
T	10.64	- -

Average k_0 value (except *) = $14.97 \times 10^{-2} \text{ ml/min}$

$$k_s = 28.14 \times 10^{-6} \text{ mole lit}^{-1} \text{ min}^{-1}$$

The results of tables 5.17 - 5.21 and table 5.13 are summarised in the following table.

TABLE 5.22

$$[K_3Fe(CN)_6] = 2.00 \times 10^{-3} \text{ M}, [O_2O_4] = 9.45 \times 10^{-6} \text{ M}$$

$$[4 - \text{Butyl morpholine}] = 2.00 \times 10^{-2} \text{ M}, \text{Temp } 35^\circ$$

$[NaOH] \times 10^2$ M	$k_s \times 10^6$ (from k_o mole lit ⁻¹ min ⁻¹)	$10^4 k_1 = \frac{k_s}{[NaOH]}$ min ⁻¹
2.50	4.47	1.78
5.00	9.21	1.84
7.50	13.91	1.85
10.00	18.52	1.85
12.50	23.27	1.82
15.00	28.14	1.87

A perusal of above table indicates that on increasing the concentration of alkali the reaction velocity increases directly. The first order constants (shown in third column of above table) at molar concentration of alkali are almost constant, which confirms first - order dependence of the reaction on alkali. The first - order kinetics in NaOH) is further confirmed when k_s values are plotted against NaOH. A straight line (Fig.5.3) with slope equal to $1.92 \times 10^{-4} \text{ min}^{-1}$

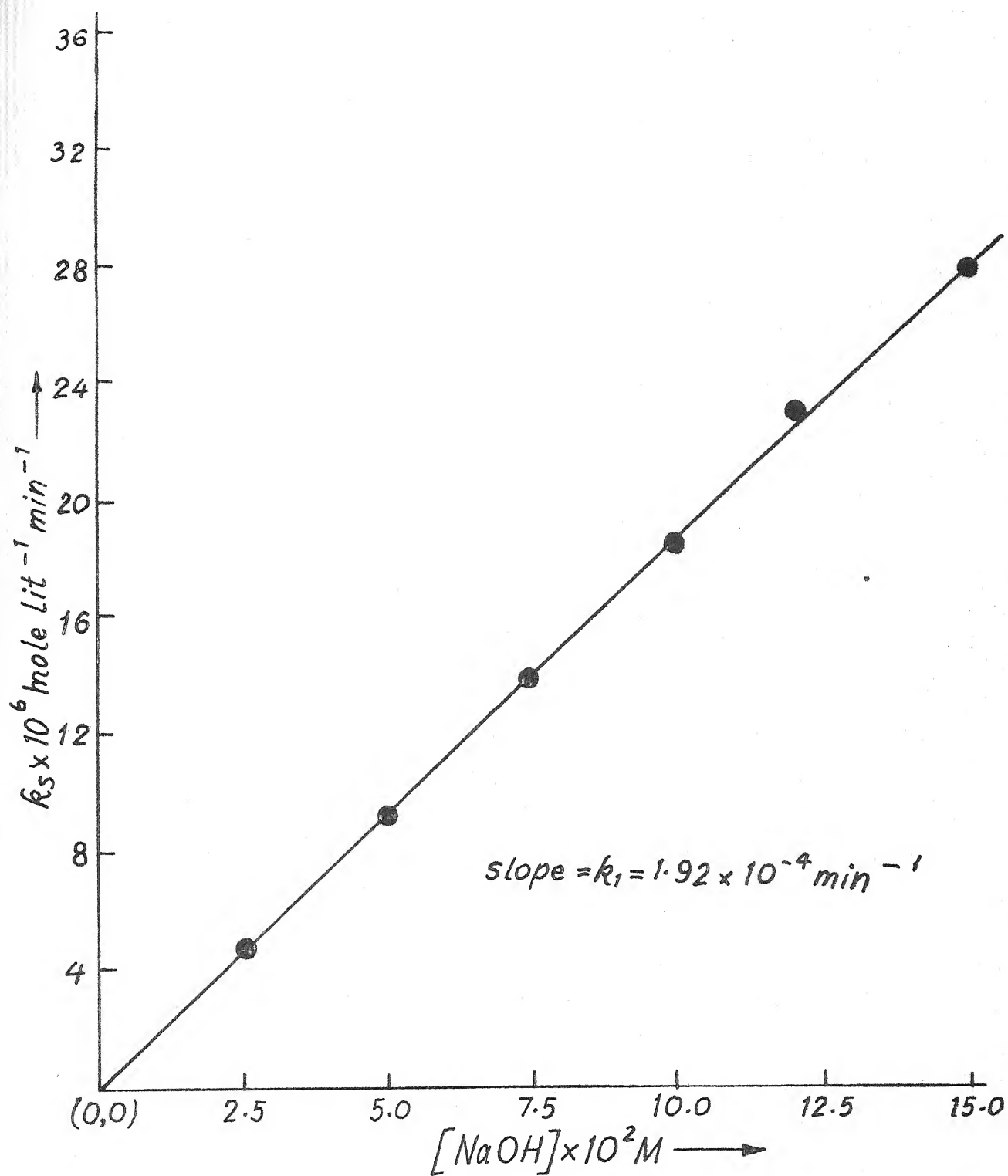


Fig. 5.3 : $[\text{K}_3\text{Fe}(\text{CN})_6] = 2.00 \times 10^{-3} \text{ M}$, $[\text{OsO}_4] = 9.45 \times 10^{-6} \text{ M}$
 $[\text{4-Butyl morpholine}] = 2.00 \times 10^{-2} \text{ M}$, Temp. 35°

is obtained. The slope gives first - order constant which resembles well with the k_1 values given in 3rd column of Table 5.22. This first order dependence of the reaction on sodium hydroxide is established.

5.4 STUDY OF EFFECT OF VARIATION OF OSMIUM TETROXIDE CONCENTRATION ON REACTION VELOCITY

In this section an attempt has been made to ascertain exactly the dependence of the reaction on osmium tetroxide concentration. In order to do so, the reaction has been studied at various concentrations of osmium tetroxide by keeping the concentration of other reactants constant. The results obtained have been shown in tables 5.23 to 5.28.

A perusal of data contained in the last column of table 5.29 shows that first - order constant k_1 (i.e. $k_1 = k_s/[O_sO_4]$) are almost constant showing a first - order dependence of the reaction on osmium tetroxide. This is further confirmed by drawing a graph between k_s values and $[O_sO_4]$. A straight line (Fig.5.4) passing through origin confirms first order in osmium tetroxide.

TABLE 5.23

Temperature 35°

$[K_3Fe(CN)_6] = 2.00 \times 10^{-3} M$, $[NaOH] = 7.50 \times 10^{-1} M$

$[4\text{-Butyl morpholine}] = 0.80 \times 10^{-2} M$, $[O_sO_4] = 4.70 \times 10^{-6} M$

Time (minute)	Volume of ceric sulphate ($9.40 \times 10^{-4} M$) in ml	$\frac{\Delta X}{\Delta t} \times 10^2$ ml/min
0	0.00	--
5	0.42	8.40*
10	0.52	2.00
15	0.62	2.00
20	0.72	2.00
30	0.92	2.00
50	1.38	2.30
80	1.98	2.00
125	2.90	2.04
200	4.42	2.02
280	6.02	2.00
T_∞	10.64	--

Average k_o value (except *) = 2.0×10^{-2} ml/min

$k_s = 3.84 \times 10^{-6}$ mole lit⁻¹ min⁻¹

TABLE 5.24

Temperature 35°

$$[K_3Fe(CN)_6] = 2.00 \times 10^{-3} \text{ M}, [NaOH] = 7.50 \times 10^{-2} \text{ M}$$

$$[4\text{-Butyl morpholine}] = 0.90 \times 10^{-2} \text{ M}, [O_2O_4] = 9.45 \times 10^{-6} \text{ M}$$

Time (minute)	Volume of Ceric sulphate ($9.40 \times 10^{-4} \text{ M}$) in ml	$\frac{\Delta X}{\Delta t} \times 10^{-2}$ ml / min
0	0.00	--
5	0.46	9.20*
10	0.66	4.00
20	1.08	4.20
30	1.48	4.00
50	2.24	3.80
75	3.24	4.00
100	4.22	3.92
150	6.14	3.84
200	8.04	3.80
T _{CP}	10.64	--

Average k_0 value (except *) = 3.95×10^{-2} ml/min

$$k_s = 7.43 \times 10^{-6} \text{ mole lit}^{-1} \text{ min}^{-1}$$

TABLE 5.25

Temperature 35°

$$[K_3Fe(CN)_6] = 2.00 \times 10^{-3} \text{ M}, [NaOH] = 7.50 \times 10^{-2} \text{ M}$$

$$[4 - \text{Butyl morpholine}] = 0.80 \times 10^{-2} \text{ M}, [O_2O_4] = 19.00 \times 10^{-6} \text{ M}$$

Time (minute)	Volume of Ceric sulphate ($9.40 \times 10^{-4} \text{ M}$) in ml	$\frac{\Delta X}{\Delta t} \times 10^2$ ml / min
0	0.00	--
5	0.62	12.40*
10	1.02	8.00
15	1.40	7.60
20	1.80	8.00
30	2.58	7.80
40	3.38	8.00
50	4.16	7.80
60	4.96	8.00
80	6.54	7.90
100	8.03	7.70
120	9.50	7.60
T_∞	10.64	--

Average k_o value (except *) = 7.84×10^{-2} ml/min

$$k_s = 14.74 \times 10^{-6} \text{ mole lit}^{-1} \text{ min}^{-1}$$

TABLE 5.26

Temperature 35°

$$[K_3Fe(CN)_6] = 2.00 \times 10^{-3} M, [NaOH] = 7.50 \times 10^{-2} M$$

$$[4\text{-Butyl morpholine}] = 0.80 \times 10^{-2} M [O_8O_4] = 19.00 \times 10^{-6} M$$

Time (minute)	Volume of ceric sulphate ($9.40 \times 10^{-4} M$) in ml	$\frac{\Delta X}{\Delta t} \times 10^2$ ml / min
0	0.0	--
5	0.62	12.40*
10	1.02	8.00
15	1.40	7.60
20	1.80	8.00
30	2.58	7.80
40	3.38	8.00
50	4.16	7.80
60	4.96	8.00
80	6.54	7.90
100	8.08	7.70
120	9.60	7.60
T_∞	10.64	--

Average k_o value (except *) = 7.84×10^{-2} ml/min

$$k_s = 14.74 \times 10^{-6} \text{ mole lit}^{-1} \text{ min}^{-1}$$

TABLE 5.27

$$[K_3Fe(CN)_6] = 2.00 \times 10^{-3} M, [NaOH] = 7.50 \times 10^{-2} M$$

$$[4\text{-Butyl morpholine}] = 0.80 \times 10^{-2} M, [O_8O_4] = 23.50 \times 10^6 M$$

Time (minute)	volume of ceric sulphate (9.40×10^{-4}) in ml	$\frac{\Delta X}{\Delta t} \times 10^2$ ml /min
0	0.00	--
5	0.80	16.00*
10	1.30	10.00
15	1.78	9.60
20	2.28	10.00
25	2.76	9.60
30	3.24	9.60
40	4.22	9.80
50	5.22	10.00
60	6.18	9.60
75	7.64	9.73
90	9.08	9.60
T_∞	10.64	--

Average k_0 value (except *) = 9.75×10^{-2} ml/min

$$k_s = 18.33 \times 10^{-6} \text{ mole lit}^{-1} \text{ min}^{-1}$$

TABLE 5.28

$$[K_3Fe(CN)_6] = 2.00 \times 10^{-3}M, [NaOH] = 7.50 \times 10^{-2}M$$

$$[4\text{-Butyl morpholine}] = 0.80 \times 10^{-2}M, [O_8O_4] = 28.00 \times 10^{-6}M$$

Time (minute)	Volume of ceric sulphate (9.40×10^{-4}) in ml)	$\frac{\Delta X}{\Delta t} \times 10^2$ ml/min
0	0.00	--
5	0.88	17.60*
10	1.48	12.00
15	2.06	11.60
20	2.64	11.60
25	3.24	12.00
30	3.82	11.60
40	5.00	11.80
50	6.18	11.80
60	7.38	12.00
75	9.16	11.86
T_∞	10.64	--

Average k_o value (except *) = 11.81×10^{-2} ml/min

$$k_s = 22.20 \times 10^{-6} \text{ mole lit}^{-1} \text{ min}^{-1}$$

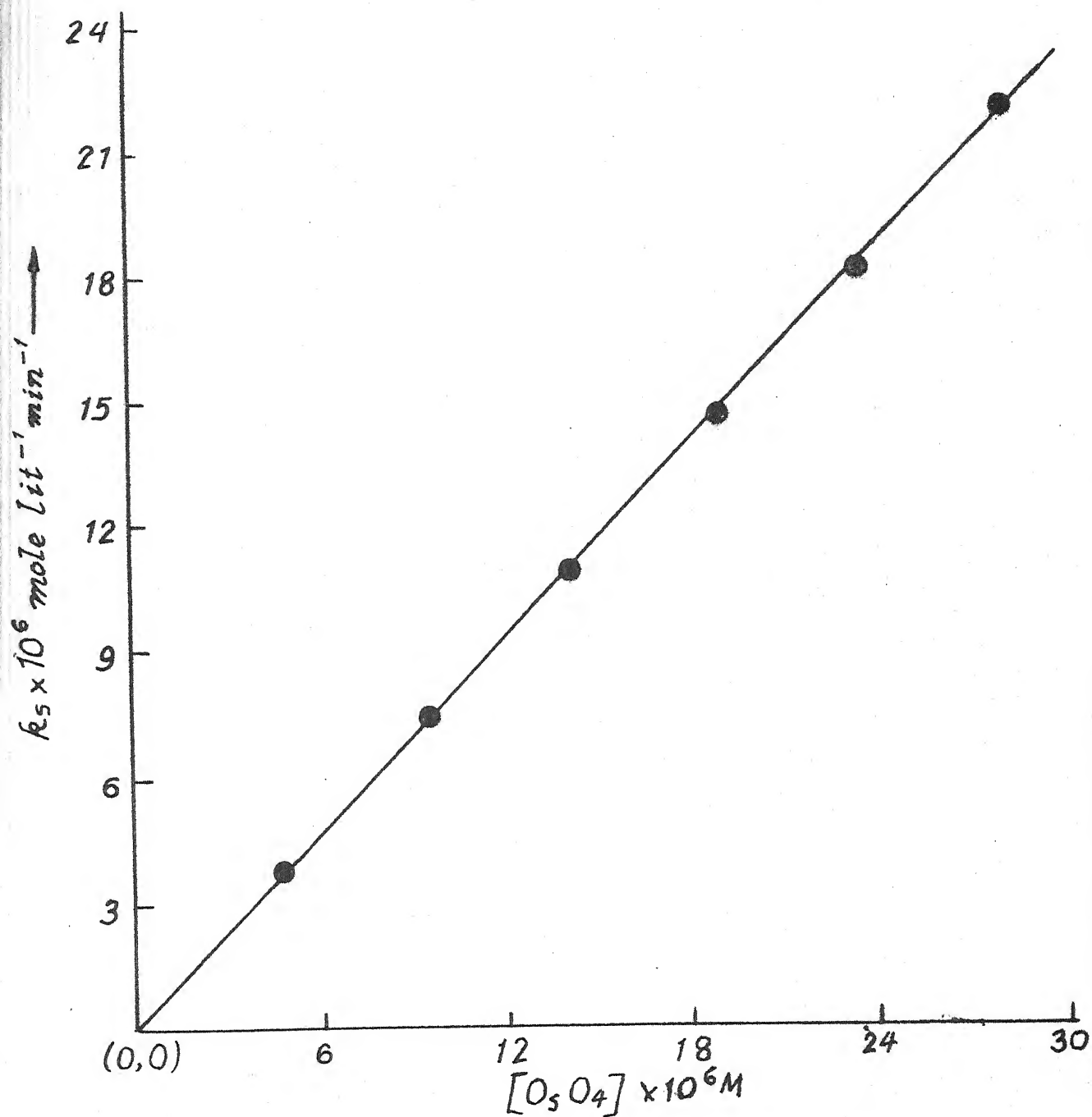


Fig.5.4 : $[K_3Fe(CN)_6] = 2.00 \times 10^{-3} M$, $[NaOH] = 7.50 \times 10^{-2} M$
 $[4\text{-Butyl morpholine}] = 0.80 \times 10^{-2} M$, Temp. 35°

The results of tables 5.23 to 5.28 are summarised in the following table.

TABLE 5.29

$$[K_3Fe(CN)_6] = 2.00 \times 10^{-3} M, [NaOH] = 7.50 \times 10^{-2} M$$

$$[4\text{-Butyl morpholine}] = 0.80 \times 10^{-2} M, \text{Temp. } 35^\circ$$

$[O_sO_4] \times 10^6$ /M	$k_s \times 10^6$ mole lit ⁻¹ min ⁻¹	$k_1 \times 10 = \frac{k_s}{[O_sO_4]}$ min ⁻¹
4.70	3.84	8.17
9.45	7.43	7.86
14.20	11.02	7.76
19.00	14.74	7.76
23.50	18.33	7.80
28.00	22.80	7.82

Average value of $k_1 = 7.86 \times 10^{-1} \text{ min}^{-1}$

5.5 STUDY OF EFFECT OF VARIATION OF IONIC STRENGTH ON REACTION RATE

In this section, an attempt has been made to investigate the effect of ionic strength of the medium on reaction velocity at fixed concentrations of other reactants. The variation of ionic strength has been affected by addition of suitable amounts of potassium chloride. The results are summarised in the following table.

TABLE 5.30

Temperature 30°

$$[K_3Fe(CN)_6] = 2.00 \times 10^{-3} \text{ M}, [NaOH] = 7.50 \times 10^{-2} \text{ M}$$

$$[4 - \text{Butyl m-orpholine}] = 1.00 \times 10^{-2} \text{ M}, [O_2O_4] = 15.60 \times 10^{-6} \text{ M}$$

$[KCl]$ M	Ionic strength (μ) M	$k_s \times 10^6$ mole lit ⁻¹ min ⁻¹
0.20	0.287	12.30
0.40	0.487	12.26
0.60	0.687	12.28
0.80	0.887	12.28
1.00	1.087	12.28
1.25	1.337	12.26
1.50	1.587	12.30

A perusal of above table shows that there is no effect of ionic strength on the reaction rate.

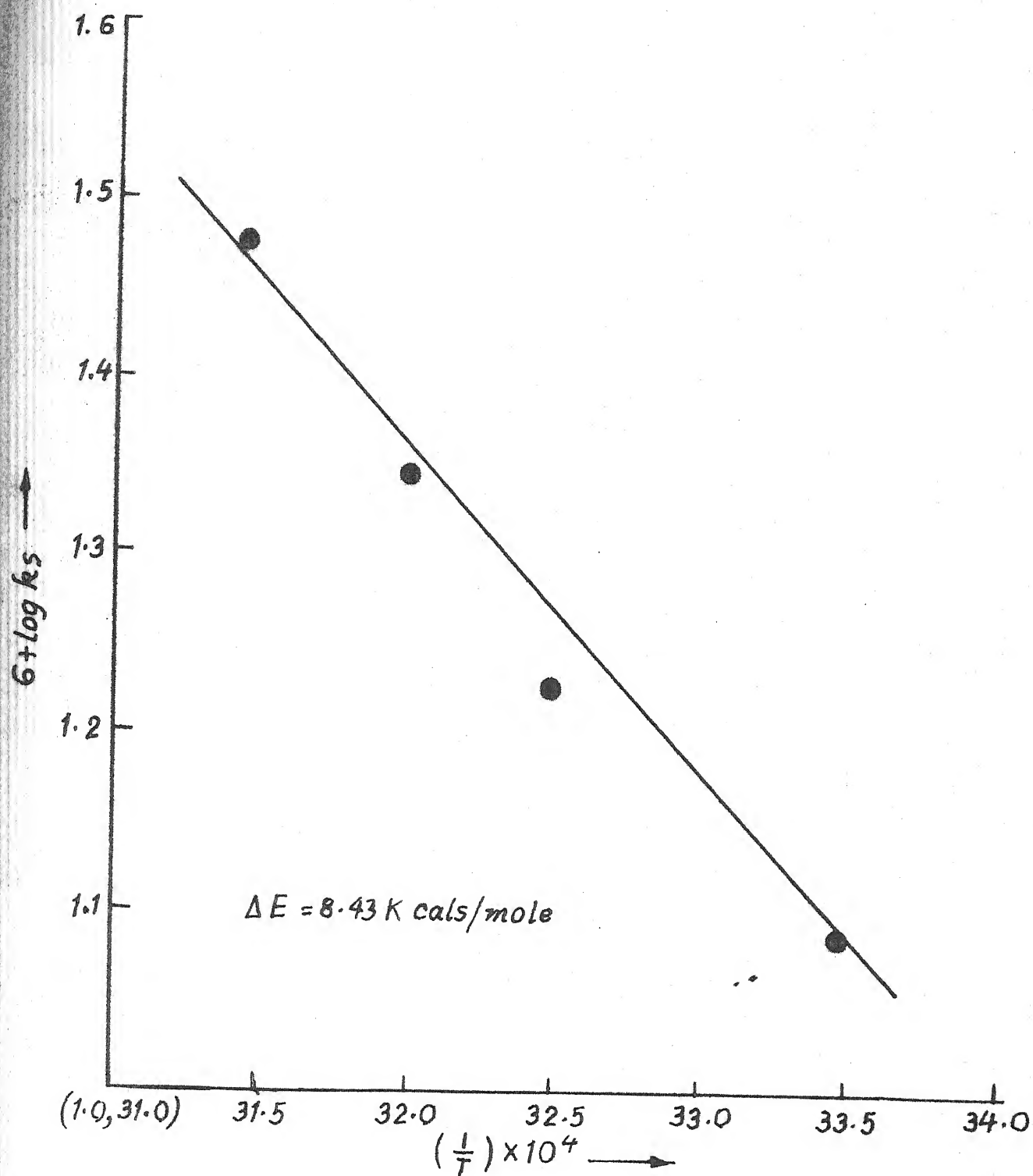


Fig. 5.5 : $[K_3Fe(CN)_6] = 2.00 \times 10^{-3} M$, $[O_5O_4] = 15.60 \times 10^{-6} M$
 $[NaOH] = 7.50 \times 10^{-2} M$, $[4\text{-Butyl morpholine}] = 1.00 \times 10^{-2} M$

5.6 EFFECT OF VARIATION OF TEMPERATURE ON REACTION VELOCITY

Here, the reaction has been studied at 35, 40 and 45°C. The reaction has already been studied at 30°C in section 5.1. The results obtained are summarised in table 5.31 when a graph is plotted between $\log k_s$ and $(1/T)$, a straight line with a slope equal to $-\Delta E/2.303R$ is obtained in accordance with Arrhenius equation.

TABLE 5.31

Summarised results showing the effect of variation of temperature on the rate of the reaction

$$[4 - \text{Butyl morpholine}] = 1.00 \times 10^{-2} \text{M},$$

$$[\text{NaOH}] = 7.50 \times 10^{-2} \text{M}$$

$$[\text{O}_3\text{O}_4] = 15.60 \times 10^{-6} \text{M}$$

Temperature °C	$[\text{K}_3\text{F}_6(\text{CN})_6] \times 10^3 \text{M}$	$k_s \times 10^6$ mole lit ⁻¹ min ⁻¹
30	2.00	12.26
35	2.00	16.68
40	2.00	22.00
45	2.00	30.24
30	2.50	12.34
35	2.50	17.12
40	2.50	22.42
45	2.50	30.76

The value of energy of activation calculated from the slope ($-\Delta E/2.303R$) of the curve (obtained on plotting a graph between $\log k_s$ and $1/T$) comes out to be 8.43 K cals/mole (Fig. 5.5).

C H A P T E R VI

KINETICS OF OSMIUM TETROXIDE CATALYSED
OXIDATION OF MORPHOLINE BUTANOL BY
ALKALINE HEXACYANOFERRATE (III)

In this chapter, an attempt has been made to study the dependence of the reaction between morpholine butanol and alkaline solution of potassium hexacyanoferrate(III) in the presence of osmium tetroxide as catalyst on each reactant i.e. on oxidant, reductant, alkali and osmium tetroxide. Effect of ionic strength of the medium has also been investigated. Here also, isolation method has been employed to determine the order of the reaction with respect to oxidant and in order to do so the concentration of oxidant has been kept comparatively smaller than that of the reducing substance. The chapter has been divided in many sections and each section deals with the dependence of the reaction on each reactant.

6.1 DETERMINATION OF ORDER OF THE REACTION WITH RESPECT TO HEXACYANOFERRATE (III)

This section deals with the determination of order of the reaction with respect to the oxidant. In order to do so, the reaction has been studied at various concentrations of the oxidant keeping the concentration of other reactants constant. The results are given in tables 6.1 to 6.7. Like previous chapter in each table k_s values ($k_s = k_o \times \frac{S}{V}$) have been given in the bottom of the tables.

TABLE 6.1

Temperature 30°C

$$[K_3Fe(CN)_6] = 0.60 \times 10^{-3}M, [NaOH] = 8.00 \times 10^{-2}M$$

$$[Morpholine\ butanol] = 1.00 \times 10^{-2}M, [O_2O_4] = 15.75 \times 10^{-6}M$$

Time (minutes)	Volume of ceric sulphate ($4.00 \times 10^{-4}M$) in ml	$\frac{\Delta X}{\Delta t} \times 10^2$ ml /min
0	0.00	--
2	1.20	60.00*
5	1.68	16.00
8	2.14	15.33
12	2.80	16.50
16	3.44	16.00
20	4.12	17.00
25	4.94	16.40
30	5.80	17.20
35	6.66	17.20
T_{∞}	7.50	--

Average value of k_o (except *) = 16.45×10^{-2} ml/min

$$k_s = k_o \frac{S}{V} = 13.16 \times 10^{-6} \text{ mole lit}^{-1} \text{ min}^{-1}$$

TABLE 6.2

Temperature 30°C

$$[K_3Fe(CN)_6] = 1.00 \times 10^{-3}M, [NaOH] = 8.00 \times 10^{-2}M$$

$$[Morpholine butanol] = 1.00 \times 10^{-2}M, [O_sO_4] = 15.75 \times 10^{-6}M$$

Time (minutes)	Volume of ceric sulphate ($4.00 \times 10^{-4}M$) in ml	$\frac{\Delta X}{\Delta t} \times 10^2$ ml / min
0	0.00	- -
5	1.80	36.00*
10	2.60	16.00
15	3.40	16.00
20	4.26	17.20
25	5.10	16.80
30	5.94	16.80
35	6.76	16.40
45	8.40	16.40
55	10.00	16.00
T_{∞}	12.50	- -

Average k_o value (except *) = 16.45×10^{-2} ml/min

$$k_s = 13.16 \times 10^{-6} \text{ mole lit}^{-1} \text{ min}^{-1}$$

TABLE 6.3

Temperature 30°C

$$[K_3Fe(CN)_6] = 1.35 \times 10^{-3} M, [NaOH] = 8.00 \times 10^{-2} M$$

$$[Morpholine butanol] = 1.00 \times 10^{-2} M, [O_s O_4] = 15.75 \times 10^{-6} M$$

Time (minutes)	Volume of ceric sulphate ($9.40 \times 10^{-4} M$) in ml	$\frac{\Delta X}{\Delta t} \times 10^2$ ml / min
0	0.00	- -
5	0.64	12.80 *
10	1.00	7.20
15	1.36	7.20
20	1.74	7.60
25	2.10	7.20
35	2.80	7.00
45	3.50	7.00
55	4.22	7.20
65	4.92	7.00
75	5.64	7.20
T_∞	7.18	- -

Average k_0 value (except *) = 7.18×10^{-2} ml/min

$$k_s = 13.50 \times 10^{-6} \text{ mole lit}^{-1} \text{ min}^{-1}$$

TABLE 6.4

Temperature 30°C

$$[K_3Fe(CN)_6] = 2.00 \times 10^{-3}, [NaOH] = 8.00 \times 10^{-2} M$$

$$[Morpholine butanol] = 1.00 \times 10^{-2} M, [O_2O_4] = 15.75 \times 10^{-6} M$$

Time (minutes)	Volume of ceric sulphate ($9.40 \times 10^{-4} M$) in ml	$\frac{\Delta X}{\Delta t} \times 10^2$ ml / min
0	0.00	- -
5	0.60	12.00*
10	0.96	7.20
15	1.32	7.20
20	1.70	7.60
25	2.06	7.20
35	2.78	7.20
45	3.52	7.40
55	4.22	7.00
70	5.28	7.06
85	6.36	7.20
T_∞	10.64	- -

Average k_o value = 7.28×10^{-2} ml/min
(except*)

$$k_s = 13.62 \times 10^{-6} \text{ mole lit}^{-1} \text{ min}^{-1}$$

TABLE 6.5

Temperature 30°C

$$[K_3Fe(CN)_6] = 2.50 \times 10^{-3} M, [NaOH] = 8.00 \times 10^{-2} M$$

$$[Morpholine\ butanol] = 1.00 \times 10^{-2} M, [O_8O_4] = 15.75 \times 10^{-6} M$$

Time (minutes)	Volume of ceric sulphate ($9.40 \times 10^{-4} M$) in ml	$\frac{\Delta X}{\Delta t} \times 10^2$ ml / min
0	0.00	--
5	0.48	9.60*
10	0.84	7.20
15	1.20	7.20
20	1.56	7.20
30	2.96	7.00
40	4.36	7.00
50	5.08	7.20
60	5.90	7.20
75	6.86	7.06
90	7.94	7.20
T_∞	13.30	--

Average k_o value (except *) = 7.14×10^{-2} ml/min

$$k_s = 13.48 \times 10^{-6} \text{ mole lit}^{-1} \text{ min}^{-1}$$

TABLE 6.6

Temperature 30°C

$$[K_3Fe(CN)_6] = 3.34 \times 10^{-3} M, [NaOH] = 8.00 \times 10^{-2} M$$

$$[Morpholine butanol] = 1.00 \times 10^{-2} M, [O_2O_4] = 15.75 \times 10^{-6} M$$

Time (minutes)	Volume of ceric sulphate ($1.88 \times 10^{-3} M$) in ml	$\frac{\Delta x}{\Delta t} = 10^2$ ml /min
0	0.00	--
5	0.40	8.00*
10	0.58	3.60
15	0.74	3.20
20	0.92	3.60
25	1.09	3.20
30	1.24	3.20
40	1.58	3.40
50	1.92	3.40
60	2.26	3.40
90	3.28	3.40
120	4.36	3.60
150	5.38	3.40
180	6.40	3.40
T_∞	8.84	--

Average k_o value (except *) = 3.40×10^{-2} ml/min

$$k_s = 12.78 \times 10^{-6} \text{ mole lit}^{-1} \text{ min}^{-1}$$

TABLE 6.7

Temperature 30°

$$[K_3Fe(CN)_6] = 5.00 \times 10^{-3} M, [NaOH] = 8.00 \times 10^{-2} M$$

$$[Morpholine\ butanol] = 1.00 \times 10^{-2} M, [O_8O_4] = 15.75 \times 10^{-6} M$$

Time (minute)	Volume of ceric sulphate ($1.88 \times 10^{-3} M$) in ml	$\frac{\Delta X}{\Delta t} \times 10^2$ ml / min
0	0.00	- -
5	0.36	7.20*
10	0.54	3.60
15	0.72	3.60
20	0.90	3.60
30	1.24	3.40
40	1.58	3.40
50	1.90	3.20
60	2.24	3.40
120	4.22	3.20
150	5.30	3.60
T_∞	13.28	- -

Average k_o value (except *) = 3.44×10^{-2} ml/min

$$k_s = 12.94 \times 10^{-6} \text{ mole lit}^{-1} \text{ min}^{-1}$$

The results of tables 6.1 to 6.7 are summarised in the following table.

TABLE 6.8

$$[\text{NaOH}] = 8.00 \times 10^{-2} \text{M}, \quad [\text{O}_2\text{O}_4] = 15.75 \times 10^{-6} \text{M}$$

$$[\text{Morpholine butanol}] = 1.00 \times 10^{-2} \text{M}, \quad \text{Temp } 30^\circ\text{C}$$

$[\text{K}_3\text{Fe}(\text{CN})_6] \times 10^3 \text{M}$	$k_s \times 10^6$ mole lit ⁻¹ min ⁻¹
0.60	13.16
1.00	13.16
1.35	13.50
2.00	13.62
2.50	13.48
3.34	12.78
5.00	12.94

$$\text{Average } k_s \text{ value} = 13.13 \times 10^{-6} \text{mole lit}^{-1} \text{min}$$

A perusal of data shown in tables 6.1 to 6.7 indicates that the reaction follows zero order kinetics in hexacyanoferrate (III). The zero - order rate constants in 3rd column of each table are almost constant. These zero - order rate constants, $k_0 \left(\frac{C \times X}{\Delta t} \right)$ are converted to standard zero - order rate constant as described in previous chapter and values are

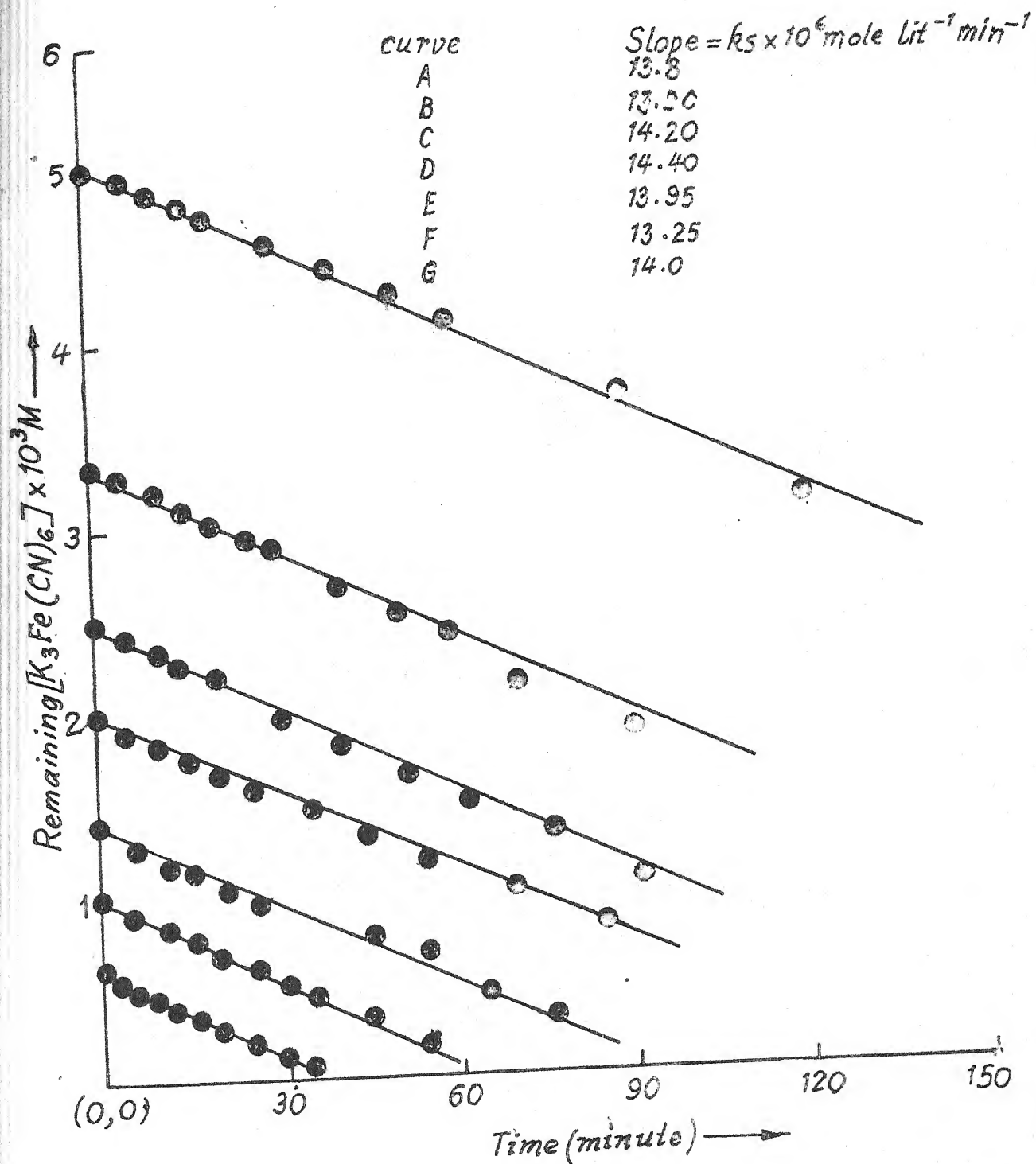


Fig. 6.1: $[Morpholine\ Butanol] = 1.00 \times 10^{-2} M$, $[O_2O_4] = 15.75 \times 10^{-6} M$
 $[NaOH] = 8.00 \times 10^{-2} M$, Temp. 30°
 $[K_3Fe(CN)_6] = 0.60 (A), 1.00 (B), 1.35 (C), 2.00 (D),$
 $2.50 (E), 3.34 (F) \text{ and } 5.00 \times 10^{-3} M (G)$

given in the bottom of each table.

The close examination of data of table 6.8 clearly indicates that k_s values (standard zero order rate constants) are almost constant showing zero - order dependence of the reaction on hexacyanoferrate (III). The average value of k_s given in the bottom of table 6.8 is quite nearer to the k_s values obtained from the slopes of the curves (graph between remaining [hexacyanoferrate (III)] and time), which shows that k_s values calculated from k_0 and obtained from slopes (Fig.6.1) are almost identical and thus zero - order kinetics in hexacyanoferrate is confirmed.

6.2 DETERMINATION OF ORDER OF REACTION WITH RESPECT TO MORPHOLINE BUTANOL

Here, an attempt has been made to ascertain the exact order of the reaction with respect to the reducing agent. In order to do so, the reaction has been studied at various initial concentrations of morpholine butanol at fixed concentration of all other reactants. Here, all also the concentrations of the reductant have been kept comparatively larger than that of hexacyanoferrate in order to allow the isolation method applicable. The results obtained have been given in Tables 6.9 to 6.14.

TABLE 6.9

Temperature 30°C

$$[K_3Fe(CN)_6] = 2.00 \times 10^{-3} M, [O_2O_4] = 10.00 \times 10^{-6} M$$

$$[Morpholine\ butanol] = 0.80 \times 10^{-2} M, [NaOH] = 8.00 \times 10^{-2} M$$

Time (minutes)	Volume of ceric sulphate ($9.40 \times 10^{-4} M$) in ml	$\frac{\Delta X}{\Delta t} \times 10^{+2}$ ml /min
0	0.00	--
5	0.40	8.00*
10	0.60	4.00
15	0.80	4.00
20	1.02	4.40
30	1.40	3.80
40	1.80	4.00
60	2.56	3.80
90	3.72	3.86
120	4.92	4.00
150	6.12	4.00
$T \infty$	10.64	--

Average value of k_0 (except*) = 3.94×10^{-2} ml/min

$$k_0 = 7.40 \times 10^{-6} \text{ mole lit}^{-1} \text{ min}^{-1}$$

TABLE 6.10

Temperature 30°C

$$[\text{K}_3\text{Fe}(\text{CN})_6] = 2.00 \times 10^{-3}\text{M}, [\text{H}_2\text{O}_4] = 10.00 \times 10^{-6}\text{M}$$

$$[\text{Morpholine butanol}] = 1.00 \times 10^{-2}\text{M} [\text{NaOH}] = 8.00 \times 10^{-2}\text{M}$$

Time (minutes)	Volume of ceric sulphate ($9.40 \times 10^{-4}\text{M}$) in ml	$\frac{\Delta X}{\Delta t} \times 10^2$ ml / min
0	0.00	--
5	0.54	10.80*
10	0.78	4.80
20	1.26	4.80
30	1.72	4.60
40	2.18	4.60
50	2.66	4.80
75	3.86	4.80
100	5.08	4.88
130	6.58	5.00
160	7.00	4.74
T_∞	10.64	--

Average k_0 value = 4.78×10^{-2} ml/min
(except*)

$$k_s = 8.98 \times 10^6 \text{ mole lit}^{-1} \text{ min}^{-1}$$

TABLE 6.11

Temperature 30°C

$$[K_3Fe(CN)_6] = 2.00 \times 10^{-3} M, [O_2O_4] = 10.00 \times 10^{-6} M$$

$$[Morpholine\ butanol] = 1.25 \times 10^{-2} M, [NaOH] = 8.00 \times 10^{-2} M$$

Time (minutes)	Volume of ceric sulphate ($9.40 \times 10^{-4} M$) in ml	$\frac{\Delta X}{\Delta t} \times 10^2 M$
0	0.00	--
5	0.70	14.00*
10	1.00	6.00
15	1.30	6.00
20	1.62	6.40
25	1.92	6.00
35	2.58	6.60
45	3.16	5.80
65	4.32	5.80
85	5.48	5.80
110	7.92	5.76
T ∞	10.64	--

Average value of k_o (except *) = 6.02×10^{-2} ml/min

$$k_s = 11.34 \times 10^{-6} \text{ mole lit}^{-1} \text{ min}^{-1}$$

TABLE 6.12

Temperature 30°C

$$[K_3Fe(CN)_6] = 2.00 \times 10^{-3} M, [O_2O_4] = 10.00 \times 10^{-6} M$$

$$[Morpholine butanol] = 1.66 \times 10^{-2} M, [NaOH] = 8.00 \times 10^{-2} M$$

Time (minute)	Volume of ceric sulphate ($9.40 \times 10^{-4} M$) in ml	$\frac{\Delta X}{\Delta t} \times 10^2$ ml / min
0	0.00	--
5	0.74	14.80*
10	1.16	8.40
15	1.56	8.00
20	1.96	8.00
25	2.38	8.40
35	3.20	8.20
45	3.98	7.80
55	4.78	8.00
70	6.00	8.14
100	8.36	7.86
T_{∞}	10.64	--

Average k_o value (except *) = 8.88×10^{-2} ml/min

$$k_s = 15.19 \times 10^{-6} \text{ mole lit}^{-1} \text{ min}^{-1}$$

TABLE 6.13

Temperature 30°C

$$[K_3Fe(CN)_6] = 2.00 \times 10^{-3} \text{ M}, [O_2O_4] = 10.00 \times 10^{-6} \text{ M}$$

$$[\text{Morpholine butanol}] = 2.50 \times 10^{-2} \text{ M}, [NaOH] = 8.00 \times 10^{-2} \text{ M}$$

Time (minutes)	Volume of ceric sulphate ($9.40 \times 10^{-4} \text{ M}$) in ml	$\frac{\Delta X}{\Delta t} \times 10^{+2}$ ml / min
0	0.00	- -
5	0.90	18.00*
10	1.52	12.40
15	2.12	12.00
20	2.72	12.40
25	3.32	12.00
30	3.92	12.00
40	5.14	12.20
50	6.36	12.20
60	7.56	11.98
T_{∞}	10.64	- -

Average k_0 value (except *) = 12.15×10^{-2} ml/min

$$k_s = 22.84 \times 10^{-6} \text{ mole lit}^{-1} \text{ min}^{-1}$$

TABLE 6.14

Temperature 30°C

$$[K_3Fe(CN)_6] = 2.00 \times 10^{-3} M, [S_2O_4^{2-}] = 10.00 \times 10^{-6} M$$

$$[Morpholine butanol] = 5.00 \times 10^{-2} M, [NaOH] = 8.00 \times 10^{-2} M$$

Time (minute)	Volume of ceric sulphate ($9.40 \times 10^{-4} M$) in ml	$\frac{\Delta X}{\Delta t} \times 10^2$ ml/min
0	0.00	--
5	1.40	28.00*
10	2.60	24.00
15	3.80	24.00
20	5.02	24.40
25	6.20	23.60
30	7.38	23.60
35	8.58	24.00
40	9.79	24.00
T_{∞}	10.64	--

Average k_o value (excent *) = 23.94×10^{-2} ml/min

$$k_s = 45.00 \times 10^6 \text{ mole lit}^{-1} \text{ min}^{-1}$$

The results of tables 6.9 to 6.14 are summarised in the following table.

TABLE 6.15

$$[K_3Fe(CN)_6] = 2.00 \times 10^{-3} M, [O_2] = 10.00 \times 10^{-6} M$$

$$[NaOH] = 8.00 \times 10^{-2} M, \text{ Temperature } 30^\circ$$

$[Morpholine\ butanol] \times 10^2$ M	$10^6 k_s$ M.L. ⁻¹ min ⁻¹	$10^4 k_1 = \frac{k_s}{[MB]}$ min ⁻¹
0.80	7.40	9.25
1.00	8.98	8.98
1.25	11.34	9.07
1.66	15.19	9.15
2.50	22.84	9.14
5.00	45.00	9.00

$$[MB] = [Morpholine\ butanol]$$

A perusal of data of table 6.15 indicates that on increasing butanol, the k_s value increases in direct proportionality showing thereby first - order kinetics with respect to morpholine[butanol]. The constant value of k_1 (obtained on dividing k_s values by $[Morpholine\ butanol]$) given in 3rd column of above table also confirms first - order dependence on morpholine butanol.

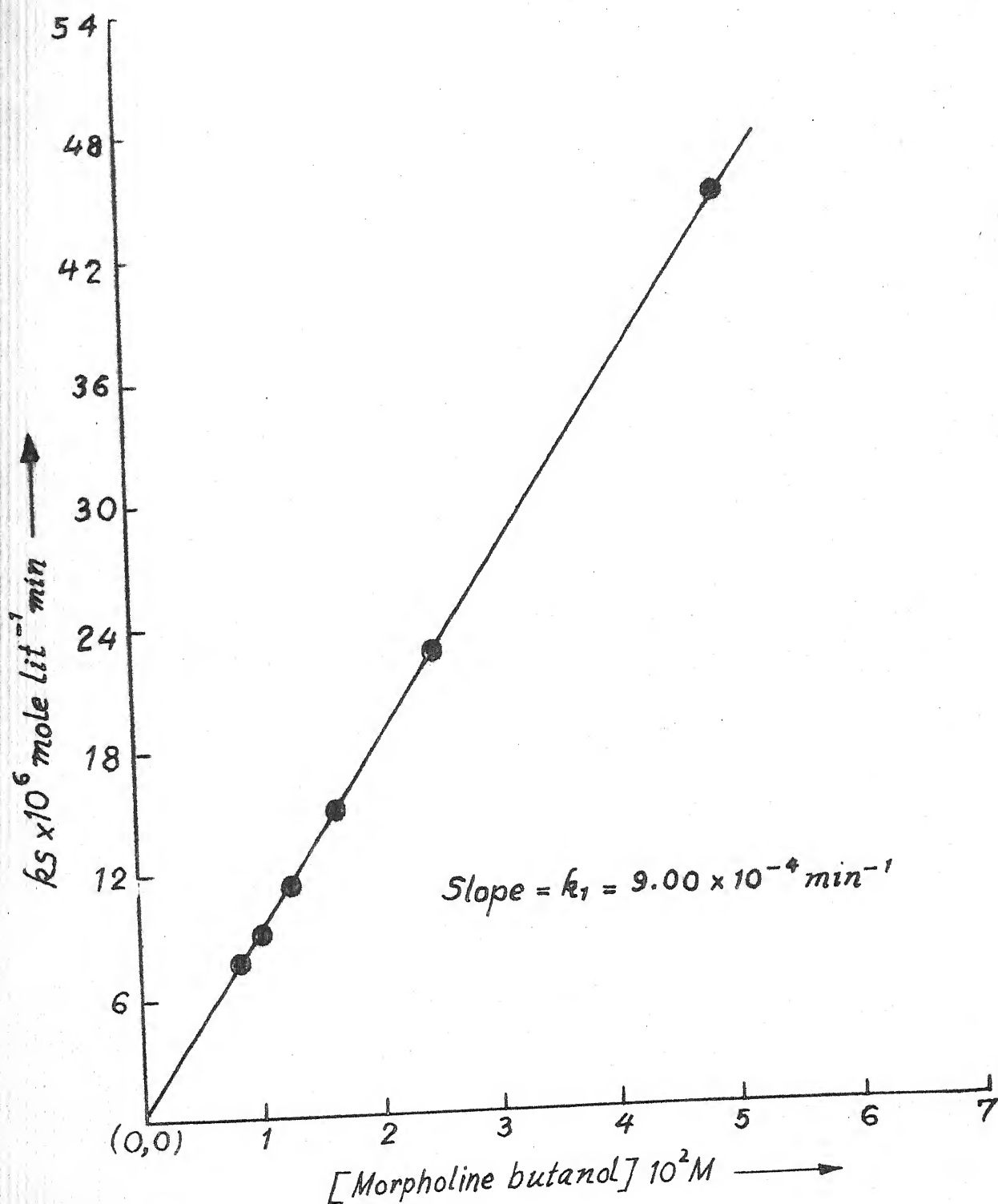


Fig. 6.2 : $[K_3Fe(CN)_6] = 2.00 \times 10^{-3} \text{ M}$, $[O_5O_4] = 10.00 \times 10^{-6} \text{ M}$
 $[NaOH] = 8.00 \times 10^{-2} \text{ M}$, Temperature 30°

In order to, further, confirm the above observation, a graph between k_s values and [Morpholine butanol] has been plotted (Fig.6.2). A straight line passing through origin and with slope equal to $9.00 \times 10^{-4} \text{ min}^{-1}$ confirms first order kinetics with respect to morpholine butanol.

6.3 DETERMINATION OF ORDER OF REACTION WITH RESPECT TO SODIUM HYDROXIDE

In order to find out the dependence of the reaction on sodium hydroxide concentration, the reaction has been studied at various concentrations of sodium hydroxide keeping the concentration of other reactants constant. It has been observed that the reaction follows first - order kinetics with respect to sodium hydroxide. The results are given in Table 6.16 to 6.21.

TABLE 6.16

Temperature 30°

$$[K_3Fe(CN)_6] = 2.00 \times 10^{-3} M, [NaOH] = 2.00 \times 10^{-2} M$$

$$[Morpholine butanol] = 1.00 \times 10^{-2} M, [O_2O_4] = 10.00 \times 10^{-6} M$$

Time (minutes)	Volume of ceric sulphate ($9.40 \times 10^{-4} M$) in ml	$\frac{\Delta X}{\Delta t} \times 10^2$ ml / min
0	0.00	- -
5	0.26	5.20*
15	0.38	1.20
25	0.50	1.20
40	0.68	1.20
70	1.02	1.13
110	1.50	1.20
150	2.00	1.25
200	2.60	1.20
260	3.32	1.20
320	4.04	1.20
T_∞	10.64	- -

Average value of k_o (except *) = 1.20×10^{-2} ml/min

$$k_s = 2.26 \times 10^{-6} \text{ mole lit}^{-1} \text{ min}^{-1}$$

TABLE 6.17

Temperature 30°C

$$[K_3Fe(CN)_6] = 2.00 \times 10^{-3} \text{ M}, [NaOH] = 4.00 \times 10^{-2} \text{ M}$$

$$[\text{Morpholine butanol}] = 1.00 \times 10^{-2} \text{ M}, [O_8O_4] = 10.00 \times 10^{-6} \text{ M}$$

Time (minutes)	Volume of ceric sulphate ($9.40 \times 10^{-4} \text{ M}$) in ml	$\frac{\Delta X}{\Delta t} \times 10^2$ ml / min
0	0.00	--
5	0.40	8.00*
10	0.52	2.40
20	0.76	2.40
35	1.14	2.53
50	1.50	2.40
80	2.20	2.33
120	3.16	2.40
160	4.12	2.40
200	5.02	2.25
T_∞	10.64	--

Average value of k_0 (except *) = $2.38 \times 10^{-2} \text{ ml/min}$

$$k_s = 4.47 \times 10^{-6} \text{ mole lit}^{-1} \text{ min}^{-1}$$

TABLE 6.18

Temperature 30°C

$$[K_3Fe(CN)_6] = 2.00 \times 10^{-3} M, [NaOH] = 6.00 \times 10^{-2} M$$

$$[Morpholine\ butanol] = 1.00 \times 10^{-2}, [O_2O_4] = 10.00 \times 10^{-6} M$$

Time (minutes)	Volume of ceric sulphate ($9.40 \times 10^{-4} M$) in ml	$\frac{\Delta X}{\Delta t} \times 10^2$ ml / min
0	0.00	--
5	0.46	9.20*
10	0.64	3.60
20	1.02	3.80
30	1.38	3.60
50	2.08	3.40
70	2.78	3.40
100	3.84	3.53
130	4.94	3.66
160	6.02	3.60
200	7.46	3.60
T_{∞}	10.64	--

Average value of k_o (except *) = 3.58×10^2 ml/min

$$k_s = 6.73 \times 10^{-6} \text{ mole lit}^{-1} \text{ min}^{-1}$$

TABLE 6.19

Temperature 30°C

$$[K_3Fe(CN)_6] = 2.00 \times 10^{-3} \text{ M}, [NaOH] = 10.00 \times 10^{-2} \text{ M}$$

$$[Morpholine butanol] = 1.00 \times 10^{-2} \text{ M}, [O_8O_4] = 10.00 \times 10^{-6} \text{ M}$$

Time (minute)	Volume of ceric sulphate ($9.40 \times 10^{-4} \text{ M}$) in ml	$\frac{\Delta X}{\Delta t} \times 10^2$ ml / min
0	0.00	- -
5	0.56	11.20*
10	0.96	6.00
15	1.16	6.00
20	1.48	6.40
30	2.10	6.20
40	2.72	6.20
50	3.32	6.00
60	3.96	6.40
80	5.22	6.30
100	6.48	6.30
T_∞	10.64	- -

Average k_0 (except *) = $6.20 \times 10^{-2} \text{ ml/min}$

$$k_s = 11.66 \times 10^{-6} \text{ mole lit}^{-1} \text{ min}^{-1}$$

TABLE 6.20

Temperature 30°C

$$[K_3Fe(CN)_6] = 2.00 \times 10^{-2} M, [NaOH] = 12.00 \times 10^{-2} M$$

$$[Morpholine butanol] = 1.00 \times 10^{-2} M, [O_2] = 10.00 \times 10^{-6} M$$

Time (minutes)	Volume of ceric sulphate ($9.40 \times 10^{-4} M$) in ml	$\frac{\Delta X}{\Delta t} \times 10^2$ ml / min
0	0.00	--
5	0.72	14.40*
10	1.10	7.60
15	1.48	7.60
20	1.84	7.20
30	2.58	7.40
40	3.28	7.00
50	3.98	7.00
60	4.70	7.20
80	6.18	7.40
100	7.69	7.50
∞	10.64	--

Average k_o value (except *) = 7.32×10^{-2} ml/min

$$k_s = 13.76 \times 10^{-6} \text{ mole lit}^{-1} \text{ min}^{-1}$$

TABLE 6.21

Temperature 30°C

$$[K_3Fe(CN)_6] = 2.00 \times 10^{-3} M, [NaOH] = 16.00 \times 10^{-2} M$$

$$[Morpholine butanol] = 1.00 \times 10^{-2} M, [O_2O_4] = 10.00 \times 10^{-6} M$$

Time (minute)	Volume of ceric sulphate ($9.40 \times 10^{-4} M$) in ml	$\frac{\Delta X}{\Delta t} \times 10^{-4}$ ml / min
0	0.00	--
5	0.80	16.00*
10	1.28	9.60
15	1.76	9.60
20	2.22	9.20
30	3.20	9.80
40	4.16	9.60
50	5.14	9.80
60	6.10	9.60
80	8.02	9.60
100	9.90	9.40
T_∞	10.54	--

Average k_o value (except *) = 9.58×10^{-2} ml/min

$$k_s = 18.01 \times 10^{-6} \text{ mole lit}^{-1} \text{ min}^{-1}$$

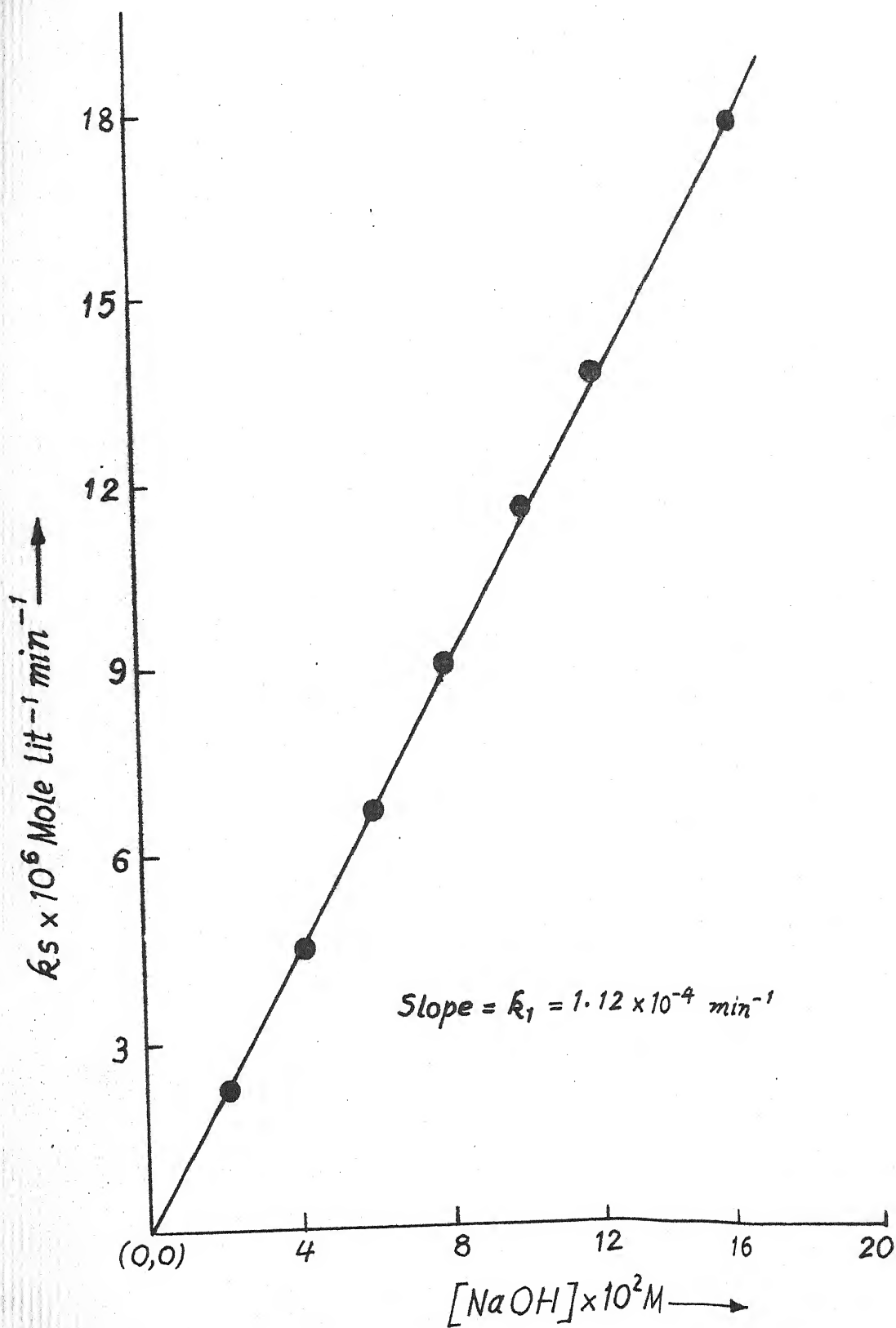


Fig. 6.3 : $[\text{K}_3\text{Fe}(\text{CN})_6] = 2.00 \times 10^{-3} \text{ M}$, $[\text{OsO}_4] = 10.00 \times 10^{-6} \text{ M}$
 $[\text{Morpholine butanol}] = 1.00 \times 10^{-2} \text{ M}$, Temp. 30°

The results of table 6.16 to 6.21 and table 6.10 are summarised in table 6.22 given below.

TABLE 6.22

$$[K_3Fe(CN)_6] = 2.00 \times 10^{-3} M, [O_2O_4] = 10.00 \times 10^{-6} M$$

$$[Morpholine butanol] = 1.00 \times 10^{-2} M, \text{Temp. } 30^\circ C$$

$[NaOH] \times 10^2$ M	$k_s \times 10^6$ mole lit ⁻¹ min ⁻¹	$10^4 k_1 = k_s / [NaOH]$ min ⁻¹
2.00	2.26	1.13
4.00	4.47	1.12
6.00	6.73	1.12
8.00	8.98	1.12
10.00	11.66	1.16
12.00	13.76	1.14
16.00	18.01	1.12

A close examination of data of above table clearly indicates that k_s values increase in direct proportionality with the increase in sodium hydroxide concentration, which proves that reaction is first order with respect to sodium hydroxide. The data contained in 3rd column of above table are almost constant showing, further, first - order dependence on sodium hydroxide concentration.

In order to, further, confirm the dependence of the reaction on sodium hydroxide, a graph between k_s values and sodium hydroxide concentration was plotted. A straight line passing through origin is obtained (Fig.6.3). The slope of the curve is $1.12 \times 10^{-4} \text{ min}^{-1}$ which proves that the reaction follows first - order kinetics with respect to sodium hydroxide concentration.

6.4 DETERMINATION OF ORDER OF REACTION WITH RESPECT TO OSMIUM TETROXIDE

In this section, an attempt has been made to determine the dependence of the reaction between morpholine butanol and hexacyanoferrate (III) on osmium tetroxide. To achieve this aim, various experiments have been performed at different initial concentrations of osmium tetroxide and the results have been recorded in tables 6.23 to 6.27. It has been observed that the reaction follows first order kinetics with respect to osmium tetroxide. In all tables in this section morpholine butanol has been referred as M.B.

TABLE 6.23

Temperature 30°C

$$[K_3Fe(CN)_6] = 2.00 \times 10^{-3}M, [NaOH] = 8.00 \times 10^{-2}M$$

$$[M.B.] = 1.00 \times 10^{-2}M, [OsO_4] = 4.00 \times 10^{-6}M$$

Time (minutes)	Volume of ceric sulphate (9.40×10^{-4}) in ml	$\frac{\Delta x}{\Delta t} \times 10^2$ ml % min
0	0.00	--
5	0.24	4.90*
15	0.42	1.80
25	0.62	2.00
40	0.90	1.86
60	1.28	1.90
90	1.88	2.00
120	2.48	2.00
160	3.28	2.00
200	4.04	1.90
250	5.04	2.00
∞	10.64	--

Average value of k_0 (except *) = 1.94×10^{-2} ml/min
 $k_0 = 3.70 \times 10^{-6}$ mole lit⁻¹ min⁻¹

TABLE 6.24

Temperature 30°C

$$[\text{K}_3\text{Fe}(\text{CN})_6] = 2.00 \times 10^{-3}\text{M}, [\text{NaOH}] = 8.00 \times 10^{-2}\text{M}$$

$$[\text{M.B.}] = 1.00 \times 10^{-2}\text{M}, [\text{O}_3\text{O}_4] = 6.50 \times 10^{-6}\text{M}$$

Time (minutes)	Volume of ceric sulphate ($9.40 \times 10^{-4}\text{M}$) in ml	$\frac{\Delta X}{\Delta t} \times 10^2$ ml / min
0	0.00	--
5	0.34	6.80*
10	0.50	3.20
20	0.82	3.20
40	1.46	3.20
60	2.06	3.00
90	3.00	3.13
120	3.90	3.00
160	5.28	3.45
200	6.56	3.20
∞	10.64	--

Average k_0 value (except *) = 3.15×10^{-2} ml/min

$$k_s = 5.92 \times 10^{-6} \text{ mole lit}^{-1}\text{min}^{-1}$$

TABLE 6.25

Temperature 30°C

$$[K_3Fe(CN)_6] = 2.00 \times 10^{-2} M, [NaOH] = 8.00 \times 10^{-2} M$$

$$[M.B.] = 1.00 \times 10^{-2} M, [O_2] = 12.50 \times 10^{-6} M$$

Time (minutes)	Volume of ceric sulphate ($9.40 \times 10^{-4} M$) in ml	$\frac{\Delta X}{\Delta t} \times 10^2$ ml / min
0	0.00	--
5	0.46	9.20*
10	0.76	6.00
15	1.08	6.40
20	1.38	6.00
30	2.00	6.20
40	3.64	6.40
50	4.26	6.20
60	4.86	6.00
80	6.10	6.20
100	7.36	6.30
$T \infty$	10.64	---

Average k_o value (except *) = 6.19×10^{-2}

$$k_s = 11.64 \times 10^{-6} \text{ mole lit}^{-1} \text{ min}^{-1}$$

TABLE 6.26

Temperature 30°C

$$[\text{K}_3\text{Fe}(\text{CN})_6] = 2.00 \times 10^{-2}\text{M}, [\text{NaOH}] = 8.00 \times 10^{-2}\text{M}$$

$$[\text{M.B.}] = 1.00 \times 10^{-2}\text{M}, [\text{O}_2\text{O}_4] = 20.00 \times 10^{-6}\text{M}$$

Time (minutes)	Volume of ceric sulphate ($9.40 \times 10^{-4}\text{M}$) in ml	$\frac{\Delta X}{\Delta t} \times 10^2$ ml /min
0	0.00	--
5	0.56	11.20*
10	1.04	9.60
15	1.50	9.20
25	2.44	9.40
35	3.40	9.60
45	4.30	9.00
60	5.70	9.33
80	7.60	9.50
100	9.58	9.90
T_∞	10.64	--

Average k_0 value (except *) = 9.44×10^{-2} ml/min

$$k_s = 17.75 \times 10^{-6} \text{ mole lit}^{-1} \text{ min}^{-1}$$

TABLE 27

Temperature 30°C

$$[\text{K}_3\text{Fe}(\text{CN})_6] = 2.00 \times 10^{-3}\text{M}, [\text{NaOH}] = 8.00 \times 10^{-2}\text{M}$$

$$[\text{M.B.}] = 1.00 \times 10^{-2}\text{M}, [\text{O}_2\text{O}_4] = 24.00 \times 10^{-6}\text{M}$$

Time (minutes)	Volume of ceric sulphate ($9.40 \times 10^{-4}\text{M}$) in ml	$\frac{\Delta X}{\Delta t} \times 10^2$ ml / min
0	0.00	--
5	0.82	16.40
10	1.34	10.40
15	1.88	10.80
20	2.40	10.40
30	3.40	10.00
40	4.46	10.60
50	5.48	10.20
60	6.50	10.20
70	7.04	10.40
80	8.04	10.00
T_{∞}	10.64	10.00

Average k_0 value (except *) = $10.33 \times 10^{-2}\text{ml/min}$

$k_s = 19.42 \times 10^{-6}\text{ mole lit}^{-1}\text{min}^{-1}$

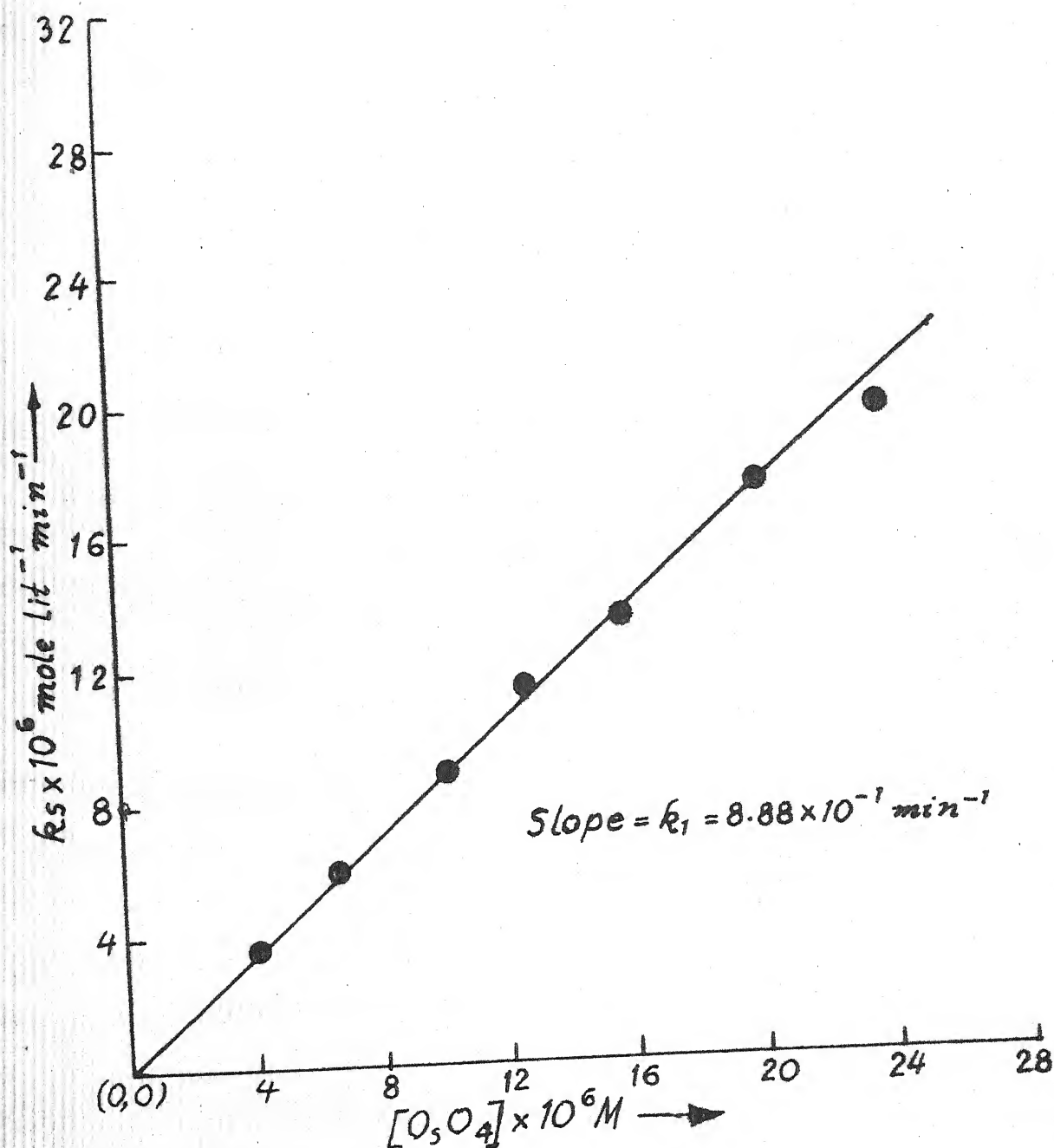


Fig. 6.4: $[K_3Fe(CN)_6] = 2.00 \times 10^{-3} M$, $[NaOH] = 8.00 \times 10^{-2} M$
 $[Morpholine \text{ butanol}] = 1.00 \times 10^{-2} M$, Temp. 30°

The results of tables 6.23 to 6.27, table 6.4 and Table 6.10 are summarised in the following table.

TABLE 6.28

$$[\text{K}_3\text{Fe}(\text{CN})_6] = 2.00 \times 10^{-3} \text{ M}, [\text{NaOH}] = 8.00 \times 10^{-2} \text{ M}$$

$$[\text{M.B.}] = 1.00 \times 10^{-2} \text{ M}, \text{ Temperature } 30^\circ\text{C}.$$

$[\text{OsO}_4] \times 10^6$ M	$k_s \times 10^6$ mole lit ⁻¹ min ⁻¹	$10 k_1 = \frac{k_s}{[\text{OsO}_4]}$ min ⁻¹
4.00	3.70	9.25
6.50	5.92	9.18
10.00	8.98	8.98
12.50	11.64	9.31
15.75	13.62	8.64
20.00	17.75	8.88
24.00	19.42	8.09

It is clear from the results of above table that k_1 of above table that k_1 values are nearly constant, showing first - order dependence of the reaction on osmium tetroxide.

The above experimental finding was, further, confirmed by plotting a graph between k_s values and concentration of osmium tetroxide (Fig.6.4). A straight line with slope equal to $8.88 \times 10^{-1} \text{ min}^{-1}$ was obtained, which shows that the order with respect to osmium tetroxide is one.

6.5 DETERMINATION OF EFFECT OF IONIC STRENGTH OF THE MEDIUM ON REACTION RATE

In most of the reactions ionic strength variation has been observed to show marked effect on reaction rate. Here, in this section an effort has been made to investigate the effect of ionic strength of the medium on reaction rate. For affecting the variation in ionic strength, suitable amounts of potassium chloride was added to the reaction mixture. The results are given in Table 6.29 in a consolidated form.

TABLE 6.29

Temperature 30°

$$[K_3Fe(CN)_6] = 2.00 \times 10^{-3} \text{ M}, [NaOH] = 8.00 \times 10^{-2} \text{ M}$$

$$[\text{Morpholine butanol}] = 1.00 \times 10^{-2} \text{ M}, [O_2O_4] = 10.00 \times 10^{-6} \text{ M}$$

$[KCl]$ M	Ionic Strength (μ) M	$k_s \times 10^6$ mole lit ⁻¹ min ⁻¹
0.20	0.28	8.98
0.40	0.48	9.00
0.60	0.68	9.02
0.75	0.83	8.96
1.00	1.08	8.99
1.25	1.33	9.00
1.50	1.58	9.02

It is clear from the above table that ionic strength variation does not effect the reaction velocity.

6.6 DETERMINATION OF EFFECT OF TEMPERATURE ON THE RATE OF REACTION

This section deals with the effect of temperature variation on reaction velocity. The reaction has been already studied at 30°C. The summarised results obtained between temperature range 30° - 45°C are given in Table 6.30. It has been observed that reaction is affected markedly by rise in temperature.

TABLE 6.30

$$[\text{NaOH}] = 8.00 \times 10^{-2} \text{ M}, \quad [\text{O}_2\text{O}_4] = 10.00 \times 10^{-6} \text{ M}$$

$$[\text{Morpholine butanol}] = 1.00 \times 10^{-2} \text{ M}$$

$[\text{K}_3\text{F}_6(\text{CN})_6] \times 10^3$	Temperature °C	$k_s \times 10^6$ mole lit ⁻¹ min ⁻¹
2.00	30	8.98
2.00	35	13.02
2.00	40	18.64
2.00	45	26.72
2.50	30	9.00
2.50	35	13.14
2.50	40	18.36
2.50	45	26.48

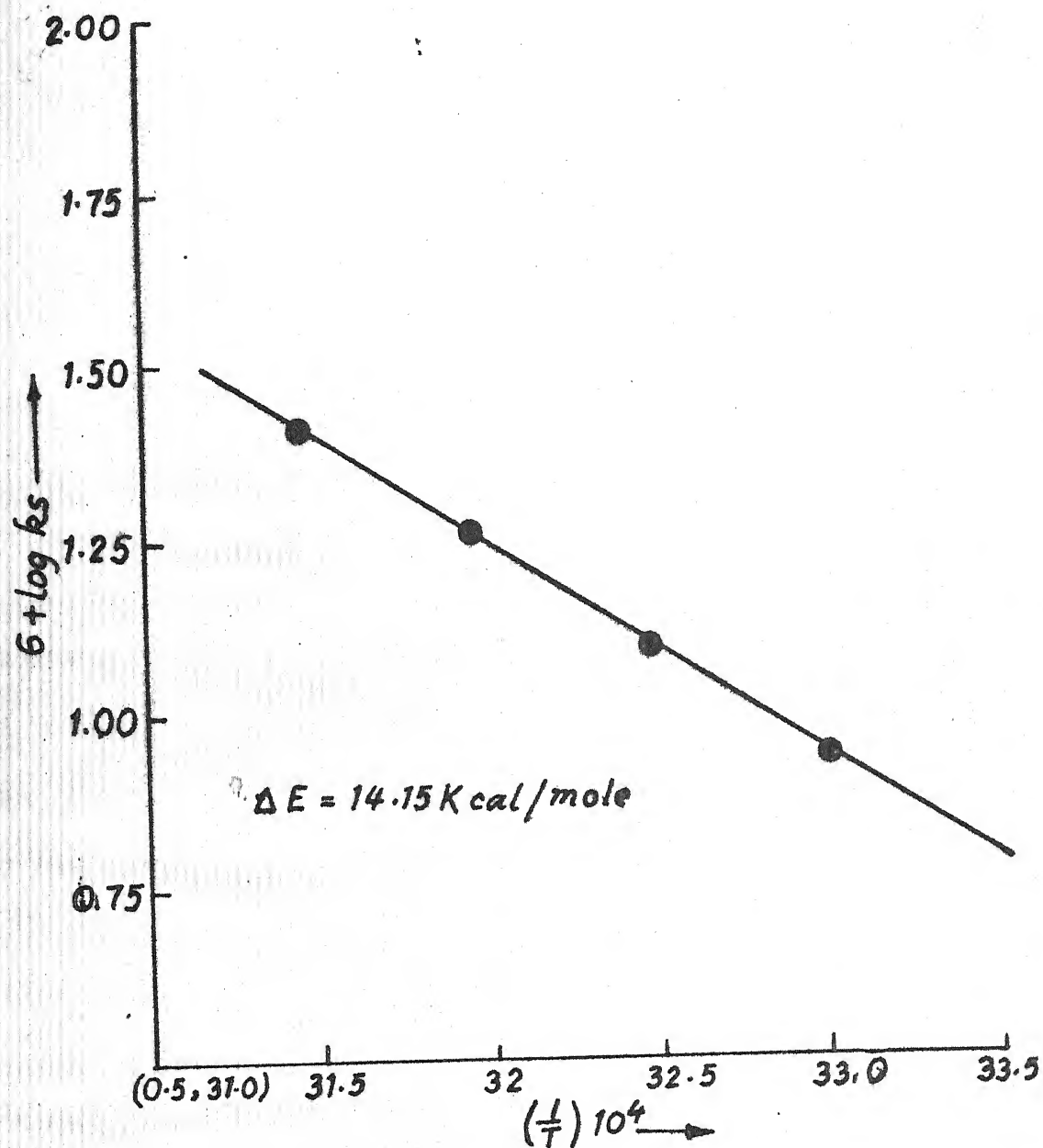


Fig. 6.5 : $[K_3Fe(CN)_6] = 2.00 \times 10^{-3} M$, $[NaOH] = 8.00 \times 10^{-2} M$
 $[O_2O_4] = 10.00 \times 10^{-6} M$, $[Morpholine \text{ butanol}] = 1.00 \times 10^{-2} M$

In order to determine the value of energy of activation, the data contained in table 6.30 were reproduced graphically by plotting a graph between $\log k_s$ and $\frac{1}{T}$ values according to Arrhenius equation. The slope of the curve gave - $\frac{\Delta E}{2.303R}$ value. Thus the value of energy of activation i.e. ΔE was calculated from the slope of the curve (Fig.6.5) and was found to be equal to 14.15 K cal/mole.

C H A P T E R - V I I

D I S C U S S I O N

It has already been stated that the main aspect of chemical kinetics is to propose a suitable mechanism by which chemical changes occur. The mechanism of a chemical process is elucidated on the basis of observations during the course of the reaction. The experimental observations are effect of various variables parameters on the rate of a reaction.

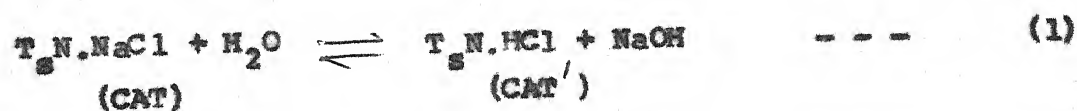
In the present thesis, two types of oxidant have ^{been} used. In third and fourth chapters, alkaline solution of chloramine - T has been employed as an oxidant in osmium tetroxide ^{Catalysed} oxidation of para - hydroxy benzoic acid (p - HBA) and meta - hydroxy benzoic acid (m - HBA). In fifth and sixth chapters, alkaline solution of hexacyanoferrate (III) has been used as an oxidant in osmium tetroxide catalysed oxidation of 4 - butyl morpholine and morpholine butanol. Here, in this chapter, an attempt would be made to propose the reaction schemes through which reactions would occur and finally rate laws for these reactions would be derived.

7.1 MECHANISM OF OSMIUM TETROXIDE CATALYSED OXIDATION
OF p - HBA AND m - HBA BY ALKALINE SOLUTION OF
CHLORAMINE - T

The main kinetic results obtained in above mentioned title reactions are given below.

- (i) Both reactions show first order dependence on chloramine - T (CAT).
- (ii) Both reactions follows first order kinetics with respect to the substrate (i.e. p - HBA and m - HBA).
- (iii) Inverse first - order with respect to alkali is observed in both cases.
- (iv) Both reactions exhibit first - order kinetics with respect to osmium tetroxide. Since both reactions follow similar kinetics, the mechanism for them is also expected to be same. Considering above kinetic data, the mechanism may be derived as given below.

In alkaline medium, the hydrolysis of chloramine-T gives the following species¹ according to the equations (1) & (2).



It is evident from above that the oxidative properties of chloramine - T in alkaline media may be due to chloramine - T (CAT) itself, p - toluene sulphochloramide (CAT')

or hypochlorite ion (ClO^-) and any one of these can react with the molecule of hydroxy benzoic acid in the rate determining step.

Now if hypochlorite ion (i.e. OCl^-) is postulated as the main oxidising species then the rate determining step must involve an interaction between neutral molecule of hydroxy benzoic acid and negatively charged hypochlorite ion. This would require positive dielectric effect. But experimental observation in this regard does not show significant effect of dielectric constant. Hence, possibility of hypochlorite ion as the main oxidising species of chloramine - T is completely ruled out.

A perusal of eqn (1) and (2) reveals that the concentrations of CAT, CAT' and OCl^- are governed by NaOH concentration. The relative concentrations of CAT and OCl^- will, increase while that of CAT' will decrease on increasing the concentration of sodium hydroxide. The experimental kinetic data show a decrease in the rate constants. On increasing NaOH concentration, which rule out the possibility of either CAT or ClO^- being the main oxidising species. It is thus clearly established that CAT' is the main reactive species in the rate determining step.²⁻⁴

Considering step (i) and eqn (5) the final rate of reaction is expressed as eqn (6).

$$-\frac{d[\text{CAT}]}{dt} = \frac{k_2 k_2' K [\text{CAT}] [\text{O}_s \text{O}_4] [\text{S}]}{(k_2 + k_2' [\text{S}]) [\text{NaOH}]} \quad \text{--- (6)}$$

where $K = K_1 [\text{H}_2\text{O}]$

k_2' is small as step (iii) is slow and rate determining ste. Thus in equality

$k_{-2} \gg k_2' [\text{S}]$ exists and eqn (6) now becomes eqn. (7)

$$-\frac{d[\text{CAT}]}{dt} = \frac{k_2 k_2' K [\text{CAT}] [\text{O}_s \text{O}_4] [\text{S}]}{k_{-2} [\text{NaOH}]} \quad \text{--- (7)}$$

The rate law (7) is in excellent agreement with kinetic observations recorded in the present thesis i.e. the rate law is in conformity with first - order dependence on chloramine-T, Osmium tetroxide, each substrate (i.e. either p - HBA or m - HBA) and inverse first order dependence on hydroxyl ion concentration. Negligible effects of ionic strength and dielectric constant also support the above mechanism.

7.2 MECHANISM OF OSMIUM TETROXIDE CATALYSED OXIDATION
OF 4 - BUTYL MORPHOLINE AND MORPHOLINE BUTANOL BY
ALKALINE HEXACYANOFERRATE (III) IONS

Experimental results obtained in osmium tetroxide catalysed oxidation of 4 -butyl morpholine and morpholine butanol by alkaline solution of hexacyanoferrate (III) are given below in a summarised form.

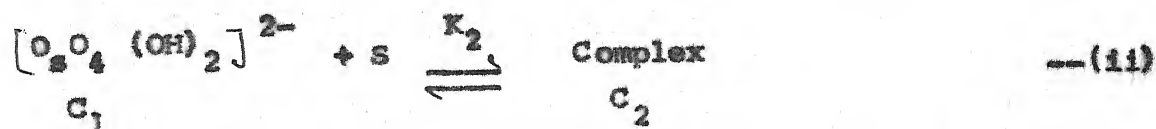
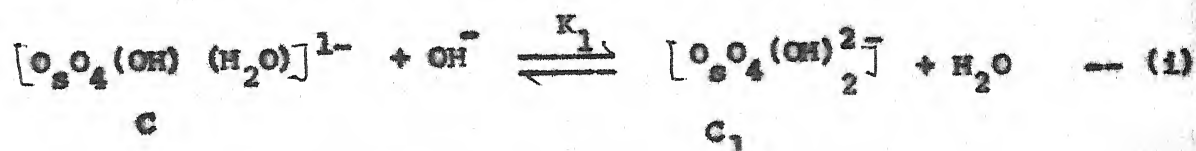
- (i) The order of the reaction with respect to hexacyanoferrate(III) was observed to be zero in both cases.
- (ii) Both the reactions followed first - order kinetics with respect to the substrate i.e. 4-butylmorpholine or morpholine butanol.
- (iii) Experimental data indicate first - order kinetics with respect to alkali.
- (iv) The reactions have been found to have first - order dependence on osmium tetroxide concentration.
- (v) Negligible effect of variation of ionic strength was observed.
- (vi) The reactions showed marked effect of temperature.

Osmium tetroxide^{5/6} has been reported to exist in alkaline medium as the octahedral complexes of the form $[\text{OsO}_4(\text{OH})(\text{HO})]^{1-}$ and $[\text{OsO}_4(\text{OH})_2]^{2-}$. The existence of the

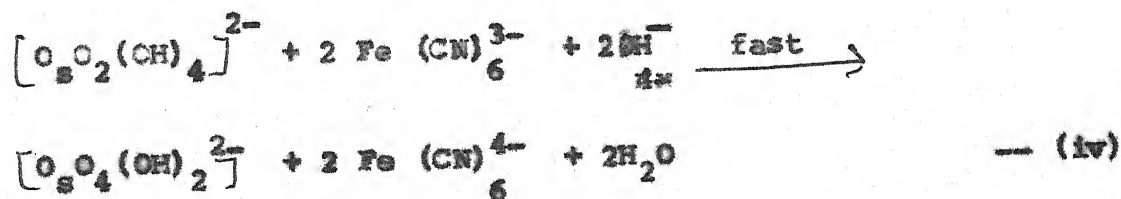
following equilibrium in alkaline medium is possible on the basis of the experimental results.



Thus it can be safely assumed that $[\text{OsO}_4(\text{OH})_2]^{2-}$ is the only reacting species acting as a catalyst with hexacyanoferrate(III). In the light of this assumption, the results mentioned above have been interpreted and a mechanism has been suggested for both reactions as these reactions follow similar kinetics.



where S is either 4 - butyl morpholine or morpholine butanol



It is clear from above scheme that total $[\text{Os}(\text{VIII})]$ at any time would be given by the equation.⁶

$$[\text{Os}(\text{VIII})]_T = [\text{C}] + [\text{C}_1] + [\text{C}_2] \quad \text{--- (1)}$$

The rate of oxidation in terms of consumption of hexacyanoferrate (III) might be written as eqn(2)

$$-d [\text{Fe (CN)}_6]^{3-} / dt = 2 \frac{d [\text{Os(VI)}]}{dt} = 2 k [\text{C}_2] \quad \text{--- (2)}$$

Now considering the equilibrium steps (I) and ii), we have

$$[\text{C}] = \frac{[\text{C}_1]}{K_1 [\text{OH}]} \quad \text{--- (3)}$$

$$\text{and } [\text{C}_2] = K_2 [\text{C}_1] [\text{S}] \quad \text{--- (4)}$$

Eqn (1) can now be written as eqn(5) with the help of eqns (3) and (4)

$$[\text{Os(VIII)}]_T = \frac{[\text{C}_1]}{K_1 [\text{OH}]} + [\text{C}_1] + K_2 [\text{C}_1] [\text{S}] \quad \text{--- (5)}$$

$$\text{or } K_1 [\text{OH}] [\text{Os(VIII)}]_T = [\text{C}_1] + [\text{C}_1] K_1 [\text{OH}] + K_1 K_2 [\text{C}_1] [\text{S}] [\text{OH}]$$

$$\text{or } [\text{C}_1] = \frac{K_1 [\text{OH}^-] [\text{Os(VIII)}]_T}{1 + K_1 [\text{OH}^-] + K_1 K_2 [\text{S}] [\text{OH}^-]} \quad \text{--- (6)}$$

considering eqns (4) and (6), we have

$$[\text{C}_2] = \frac{K_1 K_2 [\text{S}] [\text{OH}^-] [\text{Os(VIII)}]_T}{1 + K_1 [\text{OH}^-] + K_1 K_2 [\text{S}] [\text{OH}^-]} \quad \text{--- (7)}$$

According the rate of oxidation would be expressed as

$$\frac{-d [\text{Fe (CN)}_6]^{3-}}{dt} = \frac{2k K_1 K_2 [\text{S}] [\text{OH}^-] [\text{Os(VIII)}]_T}{1 + K_1 [\text{OH}^-] \{1 + K_2 [\text{S}]\}} \quad \text{--- (8)}$$

Eqn (8) can be rewritten as eqn (9) on assuming

$$K_2 [S] \ll 1$$

hence

$$\frac{-d[\text{Fe}(\text{CN})_6]^{3-}}{dt} = \frac{2k K_1 K_2 [S][\text{OH}^-][\text{Os (VIII)}]_T}{1 + K_1 [\text{OH}^-]} \quad \text{-- (9)}$$

At low concentrations of alkali as in the present thesis eqn(9) can be written as eqn (10) as inequality $1 \gg K_1 [\text{OH}^-]$ seems to be valid.

$$-d[\text{Fe}(\text{CN})_6]^{3-}/dt = 2k K_1 K_2 [S][\text{OH}^-][\text{Os (VIII)}]_T \quad \text{-- (10)}$$

Thus rate law (10) satisfactorily explains the observed kinetics in oxidation of 4 - butyl morpholine and morpholine butanol. Here the rate law/does not include hexacyanoferrate (III) term which proves that oxidation of morpholine derivatives is independent of hexacyanoferrate(III) concentration and thus follows zero order kinetics with respect to hexacyanoferrate (III) ions.

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